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(21) International Application Number: PCT/US97/16313 (22) International Filing Date: 17 September 1997 (17.09.97) (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): YANG, Jian-Zhong [CN/JP]; 2-1-215-727, Koyo-cho Naka 1-chome, Higashinada-ku, Kobe 658 (JP). MITSUMATSU, Arata [JP/JP]; 6-16-306, Midorigaoka-cho, Ashiya-shi, Hyogo 659 (JP). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: HAIR STYLING COMPOSITIONS COMPRISING NONIONIC AND AMPHOTERIC OPTICAL BRIGHTENERS (57) Abstract Disclosed is a hair styling composition comprising: (a) an effective amount of an optical brightener selected from the group consisting of a nonionic optical brightener, an amphoteric optical brightener and mixtures thereof; (b) a fixative polymer selected from the group consisting of an amphoteric fixative polymer, an anionic polymer, a cationic fixative polymer, a nonionic fixative polymer, a silicone grafted copolymer, and mixtures thereof; wherein the 3 % aqueous solution of the fixative polymer provides a viscosity of no more than about 2,000 cps; and (c) a carrier.		

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HAIR STYLING COMPOSITIONS COMPRISING NONIONIC AND AMPHOTERIC OPTICAL BRIGHTENERS

5

TECHNICAL FIELD

10 The present invention relates to a hair care composition comprising optical brighteners which alter the color of the hair, while enhancing the shininess of the hair, and protecting the hair from further damage. More specifically, the present invention relates to a hair styling composition comprising nonionic and amphoteric optical brighteners and selected fixative polymers.

15

BACKGROUND

The desire to regain the natural color and shine of damaged hair and the desire to alter the color of the hair to be more appealing are widely held. Damaged hair is perceived by the consumer as unfavorable appearances and less manageability of the hair. Such unfavorable appearances include alteration and fading of original color, less shine, and less luster.

20

A common way for alleviating the unfavorable appearances of damaged hair and to achieve appealing hair color is to dye the hair to the color desired. Dyeing the hair would provide the consumer with a stable color of hair for a relatively long period. However, dyeing the hair is generally time-consuming, cumbersome, and messy. Dyestuff may also be chemically harsh to the hair, scalp, and skin. The hair can be further damaged by dyeing. Thus, hair dye products are not suitable for daily use. Further, dyeing can leave the hair with a dull appearance, making the hair look less shiny.

25

30 Based on the foregoing, there is a need for a hair composition which can be used daily and which can alter the color of the hair, while enhancing the shininess of the hair, and protecting the hair from further damage.

30

Use of optical brighteners, or compounds otherwise described by names such as fluorescent whitening agents, fluorescent brighteners, or fluorescent dyes, in the hair care field has been known in the art, such as in United States

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Patent 3,658,985, United States Patent 4,312,855, Canadian Patent 1,255,603, United States Patent 3,577,528, Great Britain Patent Specification 1,328,108, South African Application 676,049, European Publication 87,060, and Great Britain Patent Specification 2,307,639.

5 Hair fixative polymers with different charge types are known to be useful in achieving and maintaining a desired hair style. However, when optical brighteners with a charge are mixed with hair fixative polymers of the opposite charge in a liquid media, it forms an insoluble complex, which could cause incompatibility and/or instability in the formulation. Thus, there is a desire to
10 provide a stable hair styling composition comprising optical brighteners which is compatible with a wide range of hair fixative polymers.

 None of the existing art provides all of the advantages and benefits of the present invention.

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SUMMARY

 The present invention is directed to a hair styling composition comprising:
(a) an effective amount of an optical brightener selected from the group consisting of a nonionic optical brightner, an amphoteric optical brightener and mixtures thereof; (b) a fixative polymer selected from the group consisting of an
20 amphoteric fixative polymer, an anionic fixative polymer, a cationic fixative polymer, a nonionic fixative polymer, a silicone grafted copolymer, and mixtures thereof; wherein the 3% aqueous solution of the hair fixative polymer provides a viscosity of no more than about 2,000 cps; and (c) a carrier.

 These and other features, aspects, and advantages of the present
25 invention will become evident to those skilled in the art from a reading of the present disclosure.

DETAILED DESCRIPTION

 While the specification concludes with claims particularly pointing and
30 distinctly claiming the invention, it is believed that the present invention will be better understood from the following description.

 All percentages are by weight of the total composition unless otherwise indicated. All ratios are weight ratios unless otherwise indicated. All percentages, ratios, and levels of ingredients referred to herein are based on the
35 actual amount of the ingredient, and do not include solvents, fillers, or other

materials with which the ingredient may be combined as commercially available products, unless otherwise indicated.

As used herein, "comprising" means that other steps and other ingredients which do not affect the end result can be added. This term encompasses the terms "consisting of" and "consisting essentially of".

All cited references are incorporated herein by reference in their entireties. Citation of any reference is not an admission regarding any determination as to its availability as prior art to the claimed invention.

NONIONIC AND AMPHOTERIC OPTICAL BRIGHTENERS

Optical brighteners are compounds which absorb ultraviolet light and re-emit the energy in the form of visible light. Specifically, the optical brighteners useful herein have an absorption, preferably a major absorption peak, between a wavelength of about 1nm and about 420nm, and an emission, preferably a major emission peak, between a wavelength of about 360nm and about 830nm; wherein the major absorption peak has a shorter wavelength than the major emission peak. More preferably, the optical brighteners useful herein have a major absorption peak between a wavelength of about 200nm and about 420nm, and a major emission peak between a wavelength of about 400nm and about 780nm. Optical brighteners may or may not have minor absorption peaks in the visible range between a wavelength of about 360nm and about 830nm. Optical brighteners can be described by other names in the art and in other industries, such as fluorescent whitening agents, fluorescent brighteners, and fluorescent dyes.

When applied to hair via suitable vehicles, optical brighteners herein provide benefits to the hair in three areas. First, optical brighteners herein alter the color of the hair by emitting light in the visible range. Second, optical brighteners herein enhance the shine of the hair by emitting light in the visible range. Third, optical brighteners herein protect the hair from ultraviolet light by absorbing ultraviolet light.

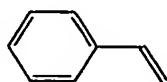
Optical brighteners in general are based on the structures of aromatic and heteroaromatic systems which provide these unique characteristics. Optical brighteners can be classified according to their charge type. The nonionic and amphoteric optical brighteners useful in the present invention are those bearing no charge or having both a positive group and a negative group. The nonionic and amphoteric optical brighteners useful in the present invention can be further

classified according to their base structures, as described hereafter. Preferable nonionic and amphoteric optical brighteners herein include polystyrylstilbenes, triazinstilbenes, hydroxycoumarins, triazoles, pyrazolines, oxazoles, pyrenes, and porphyrins.

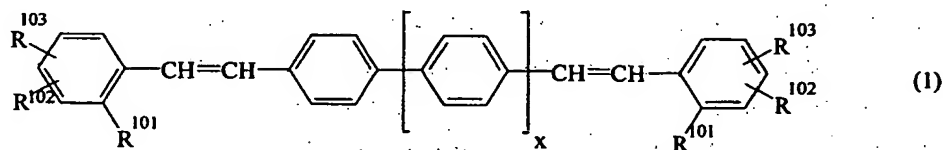
- 5 Preferably, optical brighteners herein are included in the hair care composition of the present invention at a level by weight of from about 0.001% to about 20%, more preferably from about 0.01% to about 10%.

Polystyrylstilbenes

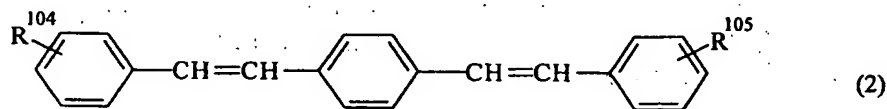
- 10 Polystyrylstilbenes are a class of compounds having two or more of the following base structure:



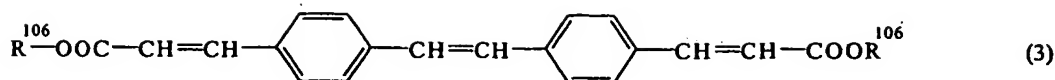
- 15 Polystyrylstilbenes useful in the present invention include those having formulae (1) (2), and (3):



- 20 wherein R¹⁰¹, R¹⁰², and R¹⁰³, independently, are H or OH; and x is 0 or 1; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; preferably x is 1, R¹⁰¹, R¹⁰², and R¹⁰³ are H; wherein the compound has a trans-coplanar orientation;



- 25 wherein R¹⁰⁴ and R¹⁰⁵, independently, are CN, COO(C₁-C₃₀-alkyl) or CON(C₁-C₄-alkyl)₂, wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; preferably R¹⁰⁴ and R¹⁰⁵ is 2-cyano; wherein the compound has a trans-coplanar orientation; and



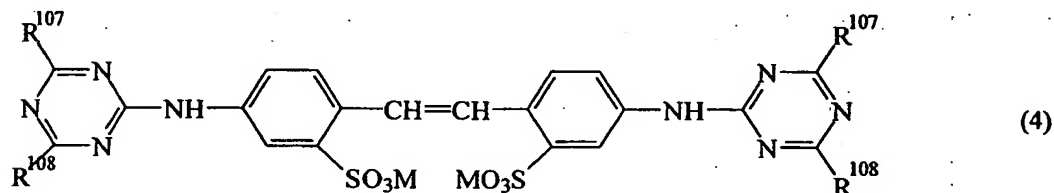
wherein each R^{106} , independently, is H, or alkyl of 1 to 30 carbons; and wherein the compound has a trans-coplanar orientation or cis-coplanar orientation, preferably a trans-coplanar orientation.

Suitable polystyrylstilbene include 1,4-bis(2-cyanostyryl)benzene (C.I. Fluorescent Brightener 199), and Ultraphor RN available from BASF.

Triazinstilbenes

Triazinstilbenes are a class of compounds having both triazin and stilbene structures in the same molecule.

Triazinstilbenes useful in the present invention include those having formulae (4):

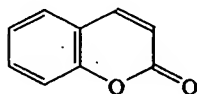


wherein R^{107} and R^{108} , independently, are phenylamino, mono- or disulfonated phenylamino, morpholino, $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$, $\text{N}(\text{CH}_3)(\text{CH}_2\text{CH}_2\text{OH})$, NH_2 , $\text{N}(\text{C}_1\text{-C}_4\text{-alkyl})_2$, OCH_3 , Cl , $\text{NH-CH}_2\text{CH}_2\text{SO}_3\text{H}$ or $\text{NH-CH}_2\text{CH}_2\text{OH}$; and M is H, Na, K, Ca, Mg, ammonium, mono-, di-, tri- or tetra- $\text{C}_1\text{-C}_{30}$ -alkylammonium, mono-, di- or tri- $\text{C}_1\text{-C}_{30}$ -hydroxyalkylammonium or ammonium that is di- or tri-substituted with by a mixture of $\text{C}_1\text{-C}_{30}$ -alkyl and $\text{C}_1\text{-C}_{30}$ -hydroxyalkyl groups, $\text{SO}_2\text{N}(\text{C}_1\text{-C}_{30}\text{-alkyl})_2$, $\text{O-}(\text{C}_1\text{-C}_{30}\text{-alkyl})$, CN , Cl , $\text{COO}(\text{C}_1\text{-C}_{30}\text{-alkyl})$, or $\text{CON}(\text{C}_1\text{-C}_{30}\text{-alkyl})_2$, CN , or alkyl of 1 to 30 carbons, wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; preferably R^{107} is 2, 5-disulfophenylamino and each R^{108} is morpholino; or each R^{107} is 2, 5-disulfophenylamino and each R^{108} is $\text{N}(\text{C}_2\text{H}_5)_2$; or each R^{107} is 3-sulfophenyl and each R^{108} is $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})$ or $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$; or each R^{107} is 4-sulfophenyl and each R^{108} is $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$; and M is sodium; wherein the compound has a trans-coplanar orientation.

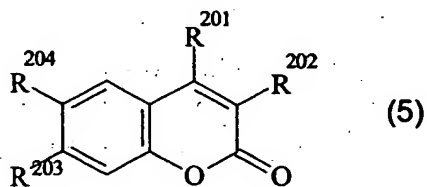
Suitable triazinstilbenes include 4,4'-bis-[(4-anilino-6-bis(2-hydroxyethyl)amino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonic acid with tradename Tinopal UNPA-GX available from Ciba Specialty Chemicals, 4,4'-bis-[(4-anilino-6-morpholine-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disodium sulfonate with tradename Tinopal AMS-GX available from Ciba Specialty Chemicals, 4,4'-bis-[(4-anilino-6-(2-hydroxyethyl)methyl amino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disodium sulfonate with tradename Tinopal 5BM-GX available from Ciba Specialty Chemicals, 4,4'-bis-[(4,6-dianilino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disodium sulfonate, 4,4'-bis-[(4-anilino-6-methylamino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disodium sulfonate, 4,4'-bis-[(4-anilino-6-ethylamino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disodium sulfonate, and 4,4'-bis(4-phenyl-1,2,3-triazol-2-yl)stilbene-2,2'-disulfonic acid.

Hydroxycoumarins

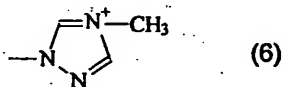
Hydroxycoumarins are a class of compounds having the following base coumarin structure and having at least one hydroxy moiety:



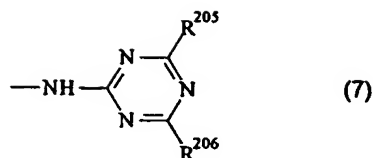
Hydroxycoumarins useful in the present invention include those having formulae (5):



wherein R²⁰¹ is H, OH, Cl, CH₃, or COOH, R²⁰² is H, phenyl, COO-C₁-C₃₀-alkyl, glucose, or a group of formula (6):



and R²⁰³ is OH, or O-C₁-C₃₀-alkyl, and R²⁰⁴ is OH or O-C₁-C₃₀ alkyl, glycoside, or a group of the following formula (7):

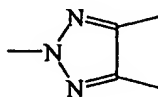


wherein R²⁰⁵ and R²⁰⁶ are independently, phenylamino, mono- or disulfonated phenylamino, morpholino, N(CH₂CH₂OH)₂, N(CH₃)(CH₂CH₂OH), NH₂, N(C₁-C₃₀-alkyl)₂, OCH₃, Cl, NH-CH₂CH₂SO₃H or NH-CH₂CH₂OH.

Suitable hydroxycoumarins include 6,7-dihydroxycoumarin available from Wako Chemicals, 4-methyl-7-hydroxycoumarin available from Wako Chemicals, 4-methyl-6,7-dihydroxycoumarin available from Wako Chemicals, esculin available from Wako Chemicals, and umbelliferone (4-hydroxycoumarin) available from Wako Chemicals.

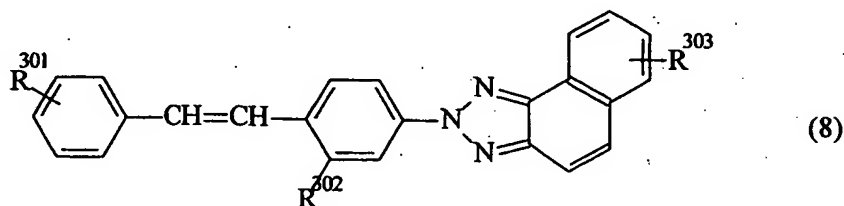
Triazoles

Triazoles are a class of compounds having the following base structure:



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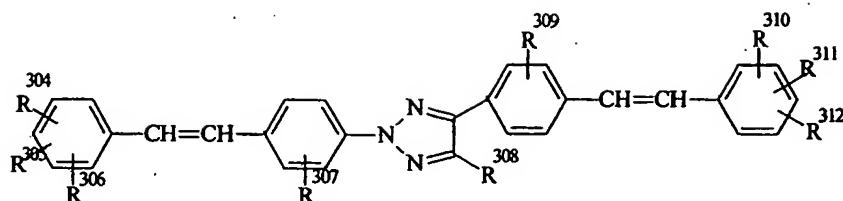
Triazoles useful in the present inventions include those having formulae (8) through (10) and (13) through (18):



20

wherein R³⁰¹ is H or Cl; R³⁰² is SO₂N(C₁-C₃₀-alkyl)₂, SO₂O-phenyl or CN; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation;

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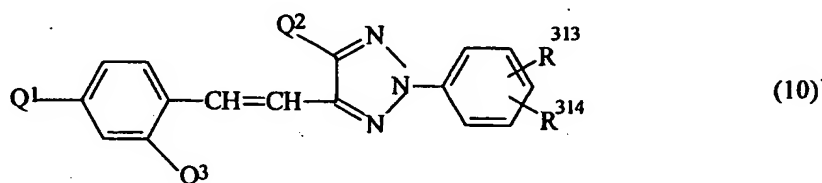


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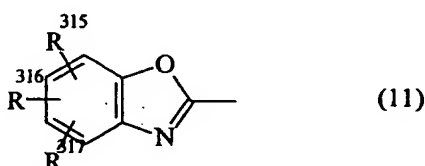
wherein each of R³⁰⁴ and R³¹⁰ independently represents H, a sulfonic acid ester or amide, a carboxylic acid ester or amide, a cyano group, a halogen atom, an unsubstituted or substituted alkylsulfonyl, arylsulfonyl, alkyl, alkoxy, aralkyl, aryl, aryloxy, aralkoxy or cycloalkyl radical, an unsubstituted or substituted 5-membered heterocyclic ring containing 2 to 3 nitrogen atoms or one oxygen atom and 1 or 2 nitrogen atoms, or together with R³⁰⁵ and R³¹¹ they represent a methylenedioxy, ethylenedioxy, methylenoxymethylenoxy, trimethylene, tetramethylene, propenylene, butenylene or butadienylene radical, each of R³⁰⁵ and R³¹¹ independently represents H, a sulfonic acid ester or amide, a carboxylic acid ester or amide, a cyano group, a halogen atom, an unsubstituted or substituted alkyl or alkoxy radical, or together with R³⁰⁴ and R³¹⁰ represent a methylenedioxy, ethylenedioxy, methylenoxymethylenoxy, trimethylene, tetramethylene, propenylene, butenylene or butadienylene radical, each of R³⁰⁶ and R³¹² independently represents H, a halogen atom or an unsubstituted or substituted alkyl radical, each of R³⁰⁷ and R³⁰⁹ independently represents H, a halogen atom, a cyano group, a sulfonic acid ester or amide, or a carboxylic acid ester or amide, and R³⁰⁸ independently represents H, a halogen atom, a cyano group, alkyl radicals preferably by hydroxy, alkoxy of 1 to 30 carbon atoms, cyano, halogen, carbalkoxy having 1 to 30 carbon atoms in the alkoxy moiety, phenyl or phenoxy; alkoxy radicals can be substituted by hydroxy, alkoxy of 1 to 30 carbon atoms, cyano, halogen, carbalkoxy having 1 to 30 carbon atoms in the alkoxy moiety, phenyl or phenoxy; phenyl, phenylalkyl or phenoxy radicals can be substituted by halogen, cyano, carboxy, carbalkoxy having 1 to 30 carbon atoms in the alkoxy moiety, sulfo, or alkyl or alkoxy each of 1 to 30 carbon atoms; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; possible cycloalkyl radicals are preferably cyclohexyl and cyclopentyl radicals which can be substituted by alkyl of 1 to 30 carbon atoms; possible 5-membered heterocyclic rings are v-triazole, oxazole or 1, 3, 4- oxdiazole radicals which can contain as substituents alkyl radicals of 1 to 4 carbon atoms, halogen, phenyl, carboxy, carbalkoxy having 1 to 30 carbon atoms in the alkoxy moiety,

cyano, benzyl, alkoxy of 1 to 30 carbon atoms, phenoxy or sulfo, whilst two adjacent substituents of the triazole and oxazole radicals together are able to form a substituted or unsubstituted fused benzene nucleus; wherein the compound has a trans-coplanar orientation;

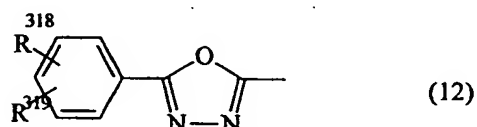
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wherein Q¹ denotes one of the ring systems (11) or (12);

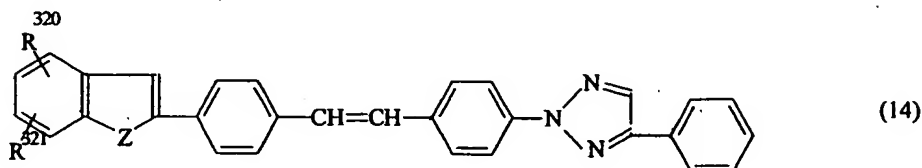
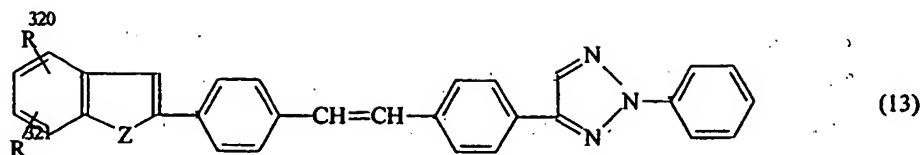


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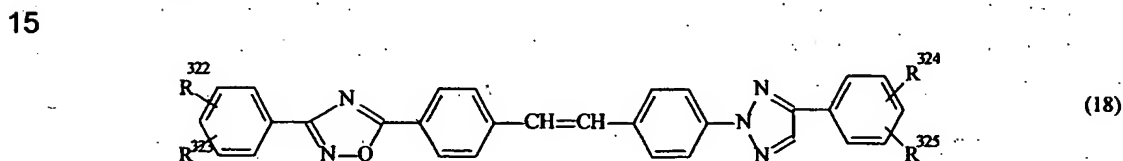
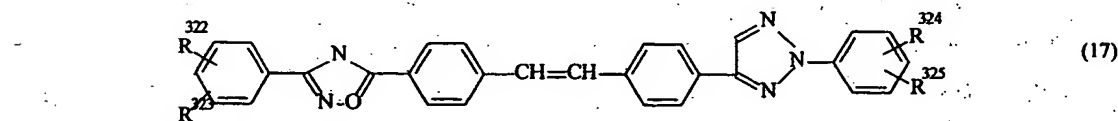
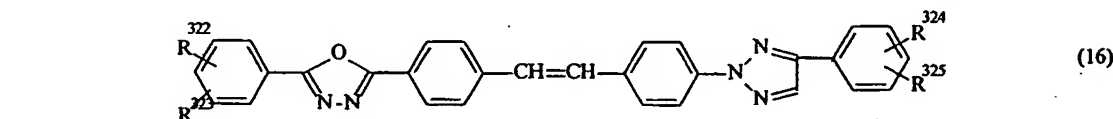
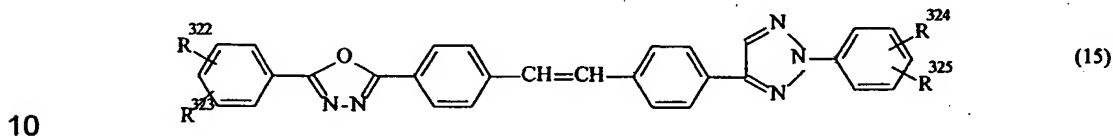


and wherein R³¹⁵ denotes H, alkyl with 1 to 30 carbon atoms, cyclohexyl, phenylalkyl with C₁-C₃₀ carbon atoms in the alkyl part, phenyl, alkoxy with 1 to 30 carbon atoms, or Cl, or, conjointly with R³¹⁶, denotes alkylene with 3 to 30 carbon atoms, R³¹⁶ denotes H or alkyl with 1 to 30 carbon atoms or, conjointly with R³¹⁵, denotes alkylene with 3 to 30 carbon atoms, R³¹⁷ denotes H or methyl, R³¹⁸ denotes H, alkyl with 1 to 30 carbon atoms, phenyl, alkoxy with 1 to 30 carbon atoms, or Cl, or, conjointly with R³¹⁹, denotes a fused benzene ring, R³¹⁹ denotes H or Cl or conjointly with R³¹⁸, denotes a fused benzene ring, R³¹³ denotes H, alkyl with 1 to 30 carbon atoms, alkoxy with 1 to 30 carbon atoms or Cl, R³¹⁴ denotes H or Cl, Q² denotes H, Cl alkyl with 1 to 30 carbon atoms or phenyl and Q³ denotes H or Cl; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation, preferably a trans-coplanar orientation;

25



- 5 wherein R³²⁰ denotes H, Cl, methyl, phenyl, benzyl, cyclohexyl or methoxy, R³²¹ denotes H or methyl and Z denotes O or S; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation, preferably a trans-coplanar orientation; and



- 15 wherein R³²² denotes H, Cl, alkyl with 1 to 30 carbon atoms, phenylalkyl with 1 to 30 carbon atoms, phenyl or alkoxy with 1 to 30 carbon atoms, or R³²² conjointly with R³²³ denotes a fused benzene radical, R³²³ denotes H or methyl or R³²³ conjointly with R³²² denotes a fused benzene radical, R³²⁴ denotes H, alkyl with 1 to 30 carbon atoms, alkoxy with 1 to 30 carbon atoms, Cl, carbalkoxy
- 20

with 1 to 30 carbon atoms or alkylsulfonyl with 1 to 30 carbon atoms and R^{325} denotes H, Cl, methyl or methoxy; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation, preferably a trans-coplanar orientation.

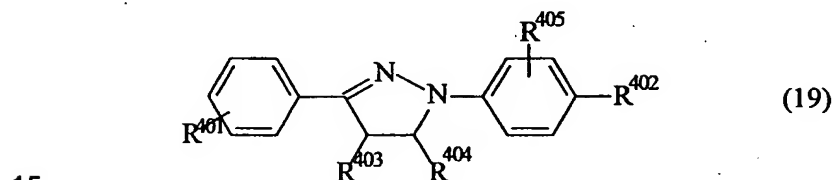
Suitable triazoles include 2-(4-styryl-3-sulfophenyl)-2H-naphtho[1,2-d]triazole (C.I. Fluorescent Brightener 46) with tradename Tinopal RBS available from Ciba Specialty Chemicals.

Pyrazolines

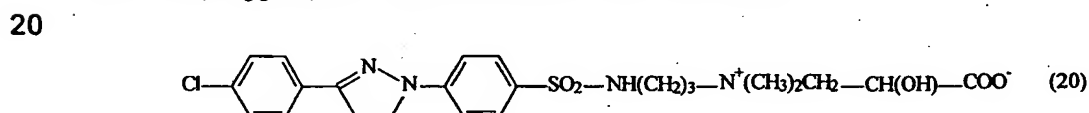
Pyrazolines are a class of compounds having the following base structure:



Pyrazolines useful in the present invention include those having formulae (19) and (20):



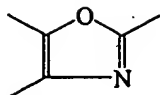
wherein R^{401} is H, Cl or $N(C_1-C_{30}\text{-alkyl})_2$, R^{402} is H, Cl, SO_2NH_2 , $SO_2NH-(C_1-C_{30}\text{alkyl})$, $COO-C_1-C_{30}\text{alkyl}$, or $SO_2C_1-C_{30}\text{alkyl}$; R^{403} and R^{404} , independently, are H, $C_1-C_{30}\text{alkyl}$ or phenyl and R^{405} is H or Cl; and



Suitable pyrazolines include 1-(4-amidosulfonylphenyl)-3-(4-chlorophenyl)-2-pyrazoline (C.I. Fluorescent Brightener 121) with tradename Blankophor DCB available from Bayer, 1-[4-(2-sulfoethylsulfonyl)phenyl]-3-(4-chlorophenyl)-2-pyrazoline, 1-[4-(2-sulfoethylsulfonyl)phenyl]-3-(3,4-dichloro-6-methylphenyl)-2-pyrazoline.

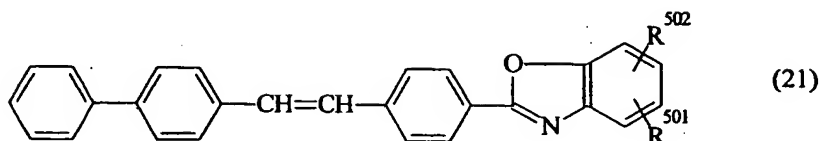
Oxazoles

Oxazoles are a class of compounds having the following base structure:

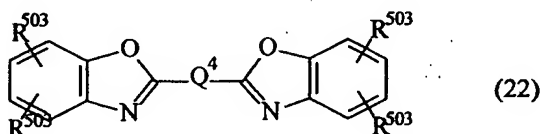


Oxazoles useful in the present inventions include those having formulae (21), (22), (23) and (24):

5

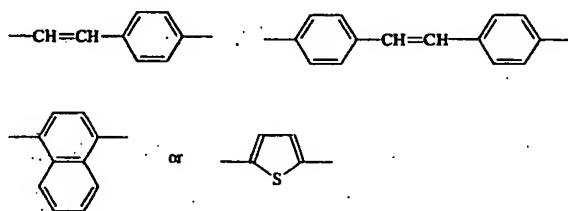


10 wherein R⁵⁰¹ and R⁵⁰², independently, are H, Cl, C₁-C₃₀alkyl or SO₂-C₁-C₃₀-alkyl, wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; preferably R⁵⁰¹ is 4-CH₃ and R⁵⁰² is 2-CH₃; wherein the compound has a trans-coplanar orientation;



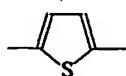
15

wherein R⁵⁰³, independently, is H, C(CH₃)₃, C(CH₃)₂-phenyl, C₁-C₃₀alkyl or COO-C₁-C₃₀alkyl, preferably H and Q⁴ is -CH=CH-;



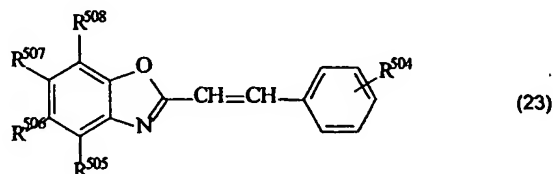
20

preferably



25 or one group R⁵⁰³ in each ring is 2-methyl and the other R⁵⁰³ is H and Q⁴ is -CH=CH-; or one group R⁵⁰³ in each ring is 2-C(CH₃)₃ and the other R⁵⁰³ is H;

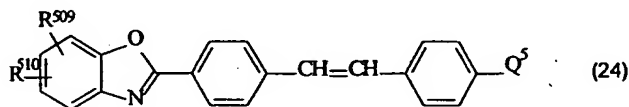
wherein the compound has a trans-coplanar orientation or cis-coplanar orientation, preferably a trans-coplanar orientation;



5

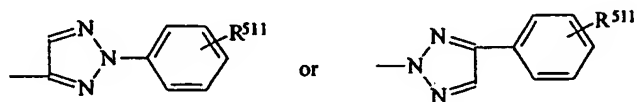
wherein R⁵⁰⁴ is CN, Cl, COO-C₁-C₃₀alkyl or phenyl; R⁵⁰⁵ and R⁵⁰⁶ are the atoms required to form a fused benzene ring or R⁵⁰⁶ and R⁵⁰⁸, independently, are H or C₁-C₃₀alkyl; and R⁵⁰⁷ is H, C₁-C₃₀alkyl or phenyl; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; preferably

10 R⁵⁰⁴ is a 4-phenyl group and each of R⁵⁰⁵ to R⁵⁰⁸ is H; wherein the compound has a trans-coplanar orientation; and



- 15 wherein R⁵⁰⁹ denotes H, Cl, alkyl with 1 to 30 carbon atoms, cyclohexyl, phenylalkyl with 1 to 3 carbon atoms in the alkyl part, phenyl or alkoxy with 1 to 30 carbon atoms, R⁵¹⁰ denotes H or alkyl with 1 to 30 carbon atoms, and Q⁵ denotes a radical;

20

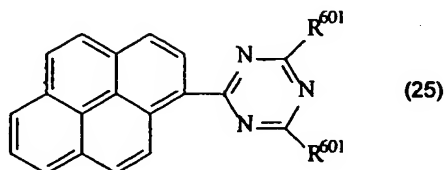


- wherein R⁵¹¹ represents H, alkyl with 1 to 30 carbon atoms, alkoxy with 1 to 30 carbon atoms, Cl, carbalkoxy with 1 to 30 carbon atoms, unsubstituted sulfamoyl or sulfamoyl which is monosubstituted or disubstituted by alkyl or hydroxyalkyl
- 25 with 1 to 30 carbon atoms or represents alkylsulfonyl with 1 to 30 carbon atoms; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation, preferably a trans-coplanar orientation.

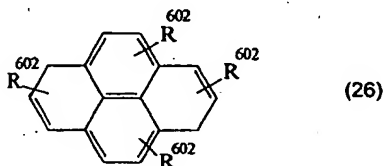
Suitable oxazoles include 4,4'-bis(5-methylbenzoxazol-2-yl)stilbene, and 2-(4-methoxycarbonylstyryl)benzoxazole.

Pyrenes

Pyrenes useful in the present invention include those having formulae (25) and (26):



wherein each R⁶⁰¹, independently, is C₁-C₃₀alkoxy; preferably methoxy; and

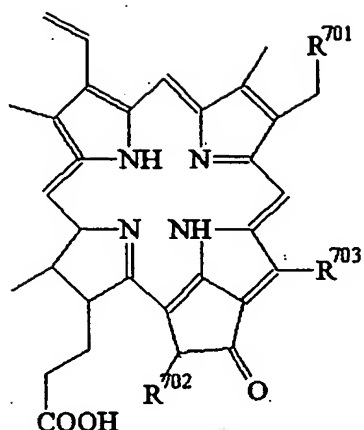


wherein each R⁶⁰², independently, is H, OH, sulfonated phenylamino, or anilino.

Porphyrins

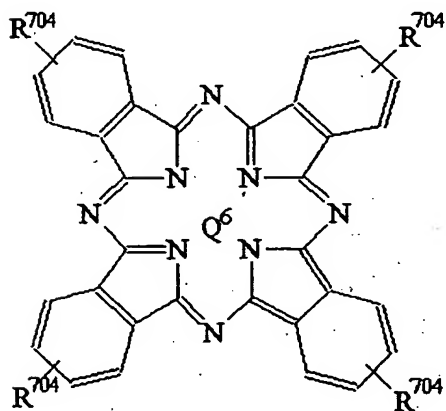
Porphyrins useful in the present invention include those having formulae (27), (28), and (29):





(28)

wherein R^{701} is CH_3 or CHO , R^{702} is H or $\text{COOC}_1\text{-C}_{30}$ alkyl, and R^{703} is H or an alkyl group having 1 to 30 carbons; and



(29)

- 5 wherein each R^{704} , independently, is H , or alkyl of 1 to 30 carbons; and Q^6 is Cu , Mg , Fe , Cr , Co , or mixtures thereof with cationic charges.

Suitable porphyrins include porphyrin available from Wako Chemicals and Copper II phthalocyanine available from Wako Chemicals.

FIXATIVE POLYMERS

- 10 The fixative polymers useful herein are those which provide a styling or setting benefit to the hair, and are selected from the group consisting of amphoteric fixative polymers, anionic fixative polymers, cationic fixative polymers, nonionic fixative polymers, silicone grafted copolymers, and mixtures thereof. The fixative polymers in this section can be distinguished from the

conditioning agent polymers and thickening polymers as mentioned below in that they have a film-forming characteristic, and that the 3% aqueous solution of fixative polymers herein provide a viscosity of no more than about 2,000 cps.

Nonionic and amphoteric optical brighteners of the present invention
5 provide benefits to the hair by depositing on the surface of the hair. Generally, styling compositions are liquid based. Thus, it is desired that the formulation containing the nonionic or amphoteric optical brightener can effectively deliver the nonionic or amphoteric optical brightener to the hair in liquid media. By selecting the fixative polymers from the group consisting of amphoteric fixative
10 polymers, anionic fixative polymers, cationic fixative polymers, nonionic fixative polymers, silicone grafted copolymers, and mixtures thereof, a styling composition which can effectively deliver the nonionic and amphoteric optical brightener and also provide good styling benefits is obtained.

It is known in the art that combining fixative polymers may enhance the
15 benefits and/or alleviate the shortcomings of the combined fixative polymers. Preferred fixative polymer combinations of the present invention include the combination of betainized amphoteric fixative polymer and non-betainized amphoteric fixative polymer, the combination of amphoteric fixative polymer and anionic fixative polymer, the combination of amphoteric fixative polymer and
20 cationic fixative polymer, and the combination of cationic fixative polymer and nonionic fixative polymer. When the combination of betainized amphoteric fixative polymer and non-betainized amphoteric fixative polymer is selected, a mousse product with good foaming characteristics can be obtained with or without propellant. Such mousse product typically contains no more than about
25 30% volatile solvent in the composition.

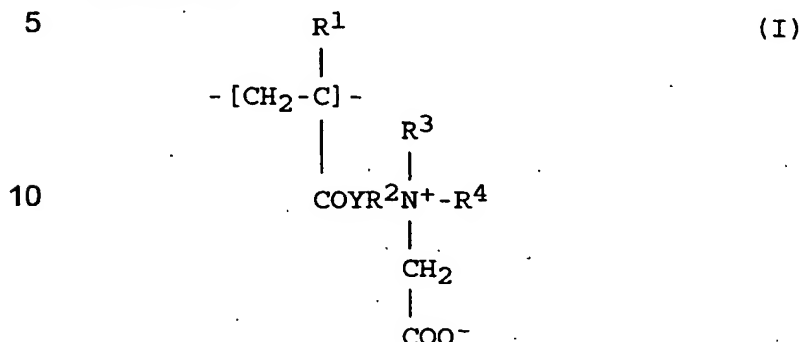
The fixative polymers are preferably included at a level of from about 0.01% to about 10% by weight of the composition. When two or more fixative polymers are used, the total preferably does not exceed about 10% by weight of the composition; more preferably, each fixative polymer does not exceed about
30 5% by weight of the composition.

Amphoteric Fixative Polymer

The amphoteric fixative polymers useful herein include betainized amphoteric fixative polymers as described in (1) and (2) below, and non-betainized amphoteric fixative polymers as described in (3) and (4) below.

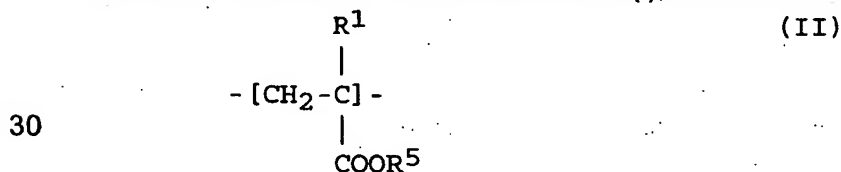
Betainized Amphoteric Fixative Polymers

(1) Useful herein are polymers of betainized dialkylaminoalkyl (meth)acrylate or dialkylaminoalkyl (meth)acrylamide containing at least units of the formula:



wherein R^1 denotes a hydrogen atom or a methyl group, R^2 denotes an alkylene group having 1 to 4 carbon atoms, Y denotes O or -NH- and R^3 and R^4 independently of one another denote hydrogen or alkyl having 1 to 4 carbon atoms, and one cationic derivative consisting of a cationic surfactant containing at least one nitrogen atom joined to one or more fatty chains and optionally quaternised, or consisting of a cationic polymer of the polyamine, polyaminopolyamide or poly-(quaternary ammonium) type, the amine or ammonium groups forming part of the polymer chain or being joined thereto. These polymers usually have a molecular weight of 500 to 2,000,000.

The amphoteric polymers containing units corresponding to the above formula (I) are generally in the form of copolymers which contain, in addition to the units of the above mentioned formula (I), at least units of the formula:



wherein R^1 is as defined above and R^5 represents an alkyl or alkenyl radical having from 4 to 24 carbon atoms or a cycloalkyl radical having from 4 to 24 carbon atoms.

It is also possible to use terpolymers, tetrapolymers or pentapolymers which contain, in addition to the units (I) and (II) defined above, units of the formula:

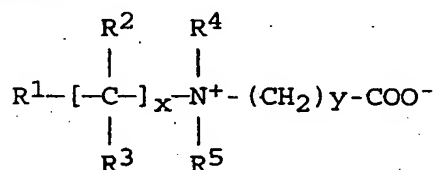


wherein R^6 preferably denotes an alkyl or alkenyl group having 1 to 3 carbon atoms and R^1 is as defined above.

The units of the formula (I) are preferably present in an amount of 25 to 45% by weight, units of the formula (II) are preferably present in an amount of 5 to 65% by weight, and units of the formula (III) are preferably present in an amount up to 50% by weight, relative to the total weight of the polymer.

A particularly preferred polymer is the copolymer containing units of the formulae (I), (II) and (III) in which Y denotes an oxygen atom, R^2 denotes the group $-\text{C}_2\text{H}_4-$, R^1 , R^3 and R^4 denote methyl, R^5 denotes an alkyl group having 4 to 18 carbon atoms and R^6 denotes an alkyl group having 1 to 3 carbon atoms. The average molecular weight of this polymer is preferably from 50,000 to 100,000. This polymer is sold under the trademark "Yukaformer" or "Diaformer" supplied by Mitsubishi Chemical Corporation.

(2) Useful herein are the betainized polymers containing zwitterionic units derived from the formula:



wherein R^1 denotes a polymerisable unsaturated group, such as an acrylate, methacrylate, acrylamide or methacrylamide group, x and y independently represent an integer from 1 to 3, R^2 and R^3 independently represent hydrogen, methyl, ethyl or propyl, and R^4 and R^5 independently represent a hydrogen atom or an alkyl radical such that the sum of the carbon atoms in R^4 and R^5 does not exceed 10.

Highly preferred betainized amphoteric polymers include commercially available material such as YUKAFORMER SM, YUKAFORMER FH, YUKAFORMER 301, YUKAFORMER 204WL, YUKAFORMER 510, YUKAFORMER M-75, YUKAFORMER R250S, Diaformer Z-SM, and Diaformer Z-W supplied by Mitsubishi Chemical Corporation.

Non-betainized Amphoteric Fixative Polymers

(3) Useful herein are the non-betainized amphoteric polymers resulting from the copolymerisation of a vinyl monomer carrying at least one carboxyl group, such as acrylic acid, methacrylic acid, maleic acid, itaconic acid, fumaric acid, crotonic acid, or alphachloroacrylic acid, and a basic monomer which is a substituted vinyl compound containing at least one basic nitrogen atom, such as dialkylaminoalkyl methacrylates and acrylates and dialkylaminoalkylmethacrylamides and -acrylamides.

(4) Useful herein are the non-betainized amphoteric polymers containing units derived from

- i) at least one monomer chosen from amongst acrylamides or methacrylamides substituted on the nitrogen by an alkyl radical,
- ii) at least one acid comonomer containing one or more reactive carboxyl groups, and
- iii) at least one basic comonomer, such as esters, with primary, secondary and tertiary amine substituents and quarternary ammonium substituents, of acrylic and methacrylic acids, and the product resulting from the quaternisation of dimethylaminoethyl methacrylate with dimethyl or diethyl sulphate.

The N-substituted acrylamides or methacrylamides which are most particularly preferred are the groups in which the alkyl radicals contain from 2 to 12 carbon atoms, especially N-ethylacrylamide, N-tert.-butylacrylamide, N-tert.-octylacrylamide, N-octylacrylamide, N-decylacrylamide and N-dodecylacrylamide and also the corresponding methacrylamides. The acid comonomers are chosen more particularly from amongst acrylic, methacrylic, crotonic, itaconic, maleic and fumaric acids and also the alkyl monoesters of maleic acid or fumaric acid in which alkyl has 1 to 4 carbon atoms.

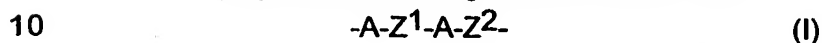
The preferred basic comonomers are aminoethyl, butylaminoethyl, N,N'-dimethylaminoethyl and N-tert.-butylaminoethyl methacrylates.

Highly preferred non-betainized amphoteric polymers include commercially available material such as octylacrylamine/acrylates/butylaminoethyl methoacrylate copolymers with the tradenames AMPHOMER, AMPHOMER SH701, AMPHOMER 28-4910, AMPHOMER LV71, and AMPHOMER LV47 supplied by National Starch & Chemical.

Cationic Fixative Polymer

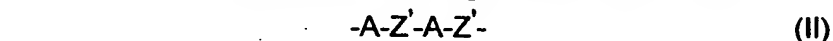
The cationic fixative polymers useful herein are:

- (1) Vinylpyrrolidone / quaternized dialkylaminoalkyl acrylate or methacrylate copolymers such as those sold under the tradename Gafquat 734 and 755N by the Gaf Corp.
- (2) Cellulose ether derivatives containing quaternary ammonium groups.
- (3) Cationic polysaccharides.
- (4) Cationic polymers chosen from the group comprising:
 - i) polymers containing units of the formula:



wherein A denotes a radical containing two amino groups, preferably a piperaziny radical, and Z^1 and Z^2 independently denote a divalent radical which is a straight-chain or branched-chain alkylene radical which contains up to about 7 carbon atoms in the main chain, is unsubstituted or substituted by one or more hydroxyl groups and can also contain one or more oxygen, nitrogen and sulphur atoms and 1 to 3 aromatic and/or heterocyclic rings, the oxygen, nitrogen and sulphur atoms generally being present in the form of an ether or thioether, sulfoxide, sulphone, sulphonium, amine, alkylamine, alkenylamine, benzylamine, amine oxide, quaternary ammonium, amide, imide, alcohol, ester and/or urethane group;

- ii) polymers containing units of the formula:



wherein A denotes a radical containing two amino groups, preferably a piperaziny radical, and Z^3 denotes the symbol Z^3 and Z^4 while denoting the symbol Z^4 at least once; Z^3 denotes a divalent radical which is a straight-chain or branched-chain alkylene or hydroxyalkylene radical having up to about 7 carbon atoms in the main chain, and Z^4 is a divalent radical which is a straight-chain or branched-chain alkylene radical which has up to about 7 carbon atoms in the main chain, is unsubstituted and substituted by one or more hydroxyl radicals and is interrupted by one or more nitrogen atoms, the nitrogen atom being substituted by an alkyl chain having from 1 to 4 carbon atoms, preferably 4 carbon atoms, which is optionally interrupted by an oxygen atom and optionally contains one or more hydroxyl groups; and

iii) the alkylation products, with alkyl and benzyl halides of 1 to 6 carbon atoms, alkyl tosylates or mesylates, and the oxidation products, of the polymers of the formulae (I) and (II) indicated above under i) and ii).

5 (5) Polyamino-polyamides prepared by the polycondensation of an acid compound with a polyamine. The acid compound can be organic dicarboxylic acids, aliphatic monocarboxylic and dicarboxylic acids containing a double bond, esters of the abovementioned acids, preferably the esters with lower alkanols having from 1 to 6 carbon atoms, and mixtures thereof. The polyamine is a bis-
10 primary or mono- or bis-secondary polyalkylene-polyamine wherein up to 40 mol% of this polyamine can be a bis-primary amine, preferably ethylenediamine, or a bis-secondary amine, preferably piperazine, and up to 20 mol% can be hexamethylenediamine.

(6) The above mentioned polyamino-polyamides can be alkylated and/or crosslinked. The alkylation can be carried out with glycidol, ethylene oxide,
15 propylene oxide or acrylamide. The crosslinking is carried out by means of a crosslinking agent such as:

- i) epihalogenohydrins, diepoxides, dianhydrides, unsaturated anhydrides and bis-saturated derivatives, in proportions of 0.025 to 0.35 mol of crosslinking agent per amine group of the polyamino-polyamide;
- 20 ii) bis-halogenohydrins, bis-azetidinium compounds, bishalogenoacyldiamines and bis-(alkyl halides);
- iii) oligomers obtained by reacting a compound chosen from the group comprising bis-halogenohydrins, bis-azetidinium compounds, bis-halogenoacyl-diamines, bis-(alkyl halides), epihalogenohydrins,
25 diepoxides and bis-unsaturated derivatives, with another compound which is a difunctional compound which is reactive towards the compound; and
- iv) the quaternisation product of a compound chosen from the compounds
30 ii) and the oligomers iii) and containing one or more tertiary amine groups which can be totally or partially alkylated with an alkylating agent preferably chosen from methyl or ethyl chlorides, bromides, iodides, sulphates, mesylates and tosylates, benzyl chloride or bromide, ethylene oxide, propylene oxide and glycidol, the crosslinking being carried out by means of 0.025 to 0.35 mol, in particular of 0.025

to 0.2 mol and more particularly of 0.025 to 0.1 mol, of crosslinking agent per amine group of the polyamino-polyamide.

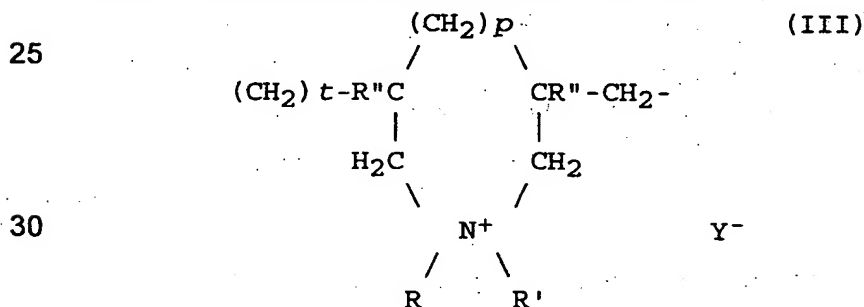
- (7) Polyamino-polyamide derivatives resulting from the condensation of a polyalkylene-polyamine with a polycarboxylic acid, followed by alkylation by means of difunctional agents, such as the adipic acid/dialkylaminohydroxyalkyl-dialkylenetriamine copolymers in which the alkyl radical contains 1 to 4 carbon atoms and preferably denotes methyl, ethyl or propyl.

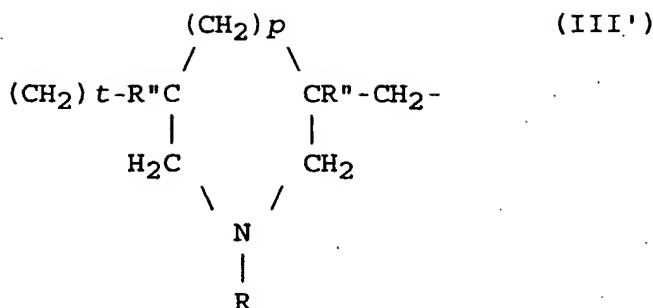
Useful polymers are adipic acid/dimethylaminohydroxypropyl-diethylenetriamine copolymers sold under the name Cartaretine F, F⁴ or F⁸ by SANDOZ.

- (8) Polymers obtained by reacting polyalkylenepolyamine containing two primary amine groups and at least one secondary amine group, with a dicarboxylic acid chosen from diglycolic acid and saturated aliphatic dicarboxylic acids having 3 to 8 carbon atoms, the molar ratio of the polyalkylene-polyamine to the dicarboxylic acid being from 0.8:1 to 1.4:1, and the resulting polyamide being reacted with epichlorohydrin in a molar ratio of epichlorohydrin to the secondary amine groups of the polyamide of from 0.5:1 to 1.8:1.

Useful polymers are those sold under the name HERCOSETT 57 by Hercules Incorporated, and that sold under the name PD 170 or DELSETTE 101 by Hercules.

- (9) Cyclic polymers generally having a molecular weight of 20,000 to 3,000,000 such as homopolymers containing, as the main constituent of the chain, units corresponding to the formula (III) or (III')



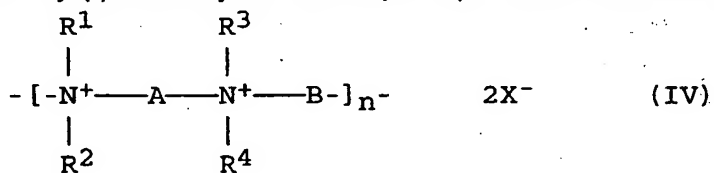


- 10 in which p and t are 0 or 1, and $p+t=1$, R'' denotes hydrogen or methyl, R and R' independently of one another denote an alkyl group having from 1 to 22 carbon-atoms, a hydroxylalkyl group in which the alkyl group preferably has 1 to 5 carbon atoms, or a lower amidoalkyl group, and R and R' can denote, together with the nitrogen atom to which they are attached, heterocyclic groups such as
- 15 piperidinyl or morpholinyl, and Y is bromide, chloride, acetate, borate, citrate, tartrate, bisulphate, bisulphite, sulphate or phosphate. Copolymers containing units of the formula III and III' may also contain units derived from acrylamide or from diacetoneacrylamide.

Amongst the quaternary ammonium polymers of the type defined above,

20 those which are preferred are the dimethyldiallylammonium chloride homopolymer sold under the name MERQUAT 100 and having a molecular weight of less than 100,000, and the dimethyldiallylammonium chloride/acrylamide copolymer having a molecular weight of more than 500,000 and sold under the name MERQUAT 550 by CALGON Corporation.

- 25 (10) Poly-(quaternary ammonium) compounds of the formula

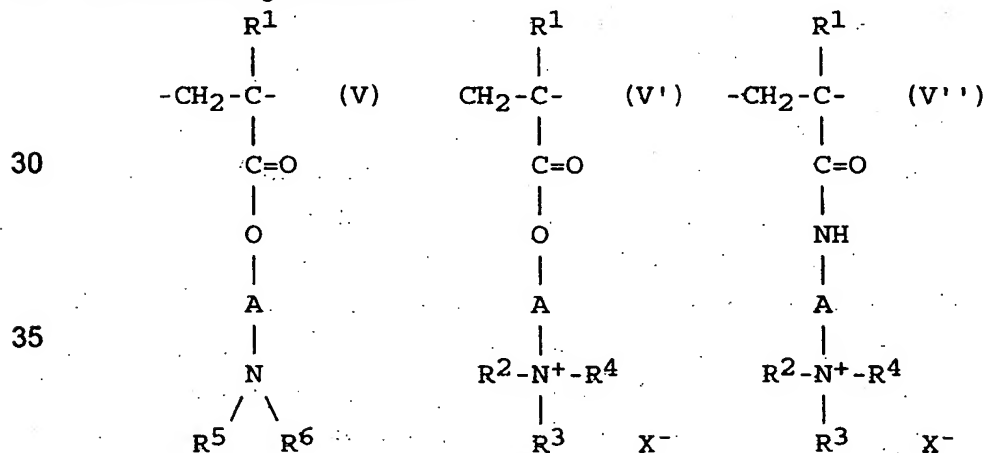


- 30 wherein R^1 , R^2 , R^3 , and R^4 are independently aliphatic, alicyclic or arylaliphatic radicals containing a maximum of 20 carbon atoms, or lower hydroxyaliphatic radicals, or alternatively, with the nitrogen atoms to which they are attached, heterocyclic rings optionally containing a second hetero-atom other than
- 35 nitrogen, or alternatively R^1 , R^2 , R^3 , and R^4 represent a group $\text{CH}_2\text{CHR}^3\text{R}^4$ wherein R^3 denoting hydrogen or lower alkyl and R^4 denoting SO , CN , $\text{CON}(\text{R}^6)_2$, COOR^5 , COR^5 , COOR^7D , or CONHR^7D ; R^5 denoting lower alkyl, R^6 denoting hydrogen or lower alkyl, R^7 denoting alkylene and D denoting a

quaternary ammonium group; A and B independently represent a polymethylene group containing from 2 to 20 carbon atoms, which can be linear or branched, saturated or unsaturated and can contain, inserted in the main chain one or more groups -CH₂-Y-CH₂- wherein Y denotes benzene, oxygen, sulfur, SO, SO₂, SS, NR⁸, N⁺(R⁹)₂X¹⁻, CHOH, NHCONH, CONR⁸, or COO; X¹⁻ denoting an anion derived from a mineral or organic acid, R⁸ denoting hydrogen or lower alkyl and R⁹ denoting lower alkyl, or alternatively A and R¹ and R³ form a piperazine ring with the two nitrogen atoms to which they are attached. If A denotes a linear or branched, saturated or unsaturated alkylene or hydroxyalkylene radical, B can also denote a group: -(CH₂)_n-CO-D-OC-(CH₂)_n-; wherein n is selected so that the molecular weight is generally between 1,000 and 100,000; and D denotes:

- i) a glycol radical of the formula -O-Z-O-, in which Z denotes a linear or branched hydrocarbon radical or a group corresponding to the formulae:
 $-\text{[CH}_2\text{-CH}_2\text{-O-]}_x\text{-CH}_2\text{-CH}_2\text{-}$ or $-\text{[CH}_2\text{-C(CH}_3\text{)H-O-]}_y\text{-CH}_2\text{-C(CH}_3\text{)H-}$
 wherein x and y denote an integer from 1 to 4, representing a definite and unique degree of polymerisation;
- ii) a bis-secondary diamine radical, such as a piperazine derivative;
- iii) a bis-primary diamine radical of the formula: -N-H-Y-NH-, in which Y denotes a linear or branched hydrocarbon radical or the divalent radical
 $-\text{CH}_2\text{-CH}_2\text{-S-S-CH}_2\text{-CH}_2\text{-}$; or
- iv) a ureylene group of the formula -N-H-CO-NH-.

(11) Homopolymers or copolymers derived from acrylic or methacrylic acid and containing at least one unit:



wherein R¹ is H or CH₃, A is a linear or branched alkyl group having 1 to 6 carbon atoms or a hydroxyalkyl group having 1 to 4 carbon atoms, R², R³ and R⁴ independently denote an alkyl group having 1 to 18 carbon atoms or a benzyl group, R⁵ and R⁶ denote H or alkyl having 1 to 6 carbon atoms and X denotes methosulphate or halide, such as chloride or bromide.

The comonomer or comonomers which can be used typically belong to the family comprising: acrylamide, methacrylamide, diacetone-acrylamide, acrylamide and methacrylamide substituted on the nitrogen by one or more lower alkyls, alkyl esters of acrylic and methacrylic acids, vinylpyrrolidone and vinyl esters.

Useful polymers are Quaternium 38, 37, 49 and 42 in the CTFA, acrylamide/beta-methacryloyloxyethyl-trime-thylammonium methosulphate copolymers sold under the names Teten 205,210,220 and 240 by Hercules, and aminoethylacrylate phosphate/acrylate copolymer sold under the name Catrex by National Starch & Chemicals, and the crosslinked graft cationic copolymers having a molecular weight of 10,000 to 1,000,000, and preferably of 15,000 to 500,000, and resulting from the copolymerisation of: at least one cosmetic monomer, dimethylaminoethyl methacrylate, polyethylene glycol and a polyunsaturated crosslinking agent, such as those mentioned in the CTFA dictionary under the name AMODIMETHICONE, such as the product marketed as a mixture with other ingredients under the name DOW CORNING 929 cationic emulsion.

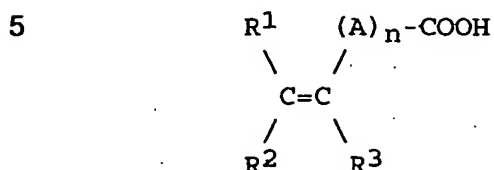
(12) Other cationic polymers which can be used are polyalkyleneimines, in particular polyethyleneimines, polymers containing vinylpyridine units or vinylpyridinium units in the chain, condensates of polyamines and of epichlorohydrin, poly-(quaternary ureylenes) and chitin derivatives.

Highly preferred cationic fixative polymers include commercially available material such as Polyquaternium 4 under the tradenames CELQUAT H100 and CELQUAT L200 supplied by National Starch & Chemicals, and Polyquaternium 11 under the tradename GAFQUAT 755N supplied by ISP.

Anionic Fixative Polymer

The anionic fixative polymers useful herein include polymers containing units derived from carboxylic, sulphonic or phosphoric acid and usually have a molecular weight of 500 to 5,000,000. These polymers are water-soluble polymers, it being possible for this solubility to be obtained by neutralisation.

The carboxylic acid groups can be provided by unsaturated monocarboxylic or dicarboxylic acids, such as those corresponding to the formula:



wherein n is 0 or an integer from 1 to 10, A denotes a methylene group optionally joined to the carbon atom of the saturated group, or to the adjacent methylene group in the case where n is greater than 1, via a heteroatom, such as oxygen or sulphur, R¹ denotes a hydrogen atom or a phenyl or benzyl group, R² denotes a hydrogen atom, a lower alkyl group or a carboxyl group and R³ denotes a hydrogen atom, a lower alkyl group, CH₂COOH, or a phenyl or benzyl group.

According to the invention, the preferred polymers containing carboxylic acid groups are:

(1) Homopolymers or copolymers of acrylic or methacrylic acid or salts thereof, and in particular, the products sold under the name VERSICOL E or K, and ULTRAHOLD by BASF and under the name DARVAN No. 7 by Van der Bilt; acrylic acid/acrylamide copolymers sold in the form of their sodium salt under the name RETEN 421, 423 or 425 by HERCULES; and the sodium salts of polyhydroxycarboxylic acids, sold under the name HYDAGEN F by HENKEL.

(2) Copolymers of acrylic or methacrylic acid with a monoethylenic monomer, such as ethylene, styrene, a vinyl or allyl ester or acrylic or methacrylic acid ester, optionally grafted onto a polyalkylene glycol, such as polyethylene glycol, and optionally crosslinked. Other such copolymers contain an optionally N-alkylated and/or N-hydroxylated acrylamide unit in their chain, such as those sold under the name QUADRAMER 5 by American Cyanamid.

(3) Copolymers derived from crotonic acid, such as those containing, in their chain, vinyl acetate or propionate units and optionally other monomers such as allyl or methallyl esters, a vinyl ether or a vinyl ester of a saturated linear or branched carboxylic acid with a hydrocarbon chain of at least 5 carbon atoms, if appropriate, for these polymers to be grafted and crosslinked, or also a vinyl, allyl or methallyl ester of an α- or β-cyclic carboxylic acid. Included in this class are

those with the tradename RESYN 28-2930, 28-2913, and 28-1310 sold by National Starch & Chemicals.

(4) Polymers derived from maleic, fumaric and itaconic acids or anhydrides with vinyl esters, vinyl ethers, vinyl halides, phenylvinyl derivatives, acrylic acid and its esters, such as those sold under the name GANTREZ A, SP, and ES by ISP. Other polymers included in this class are copolymers of maleic, citraconic and itaconic anhydrides with an allyl or methallyl ester optionally containing an acrylamido or methacrylamido group, or with an α -olefine, acrylic or methacrylic acid ester, acrylic or methacrylic acid or vinylpyrrolidone unit in their chain; the anhydride groups can be monoesterified or monoamidified.

(5) Polyacrylamides containing carboxylate groups. Polymers comprising sulphonic groups include polymers containing vinylsulphonic, styrenesulphonic, lignosulphonic or naphthalenesulphonic units. These polymers are chosen, in particular, from amongst:

- i) Polyvinylsulphonic acid salts having a molecular weight of 1,000 to 100,000, and also copolymers with an unsaturated comonomer, such as acrylic or methacrylic acid or an ester thereof and also substituted or unsubstituted acrylamide or methacrylamide, vinyl esters, vinyl ethers and vinylpyrrolidone.
- ii) Polystyrenesulphonic acid salts, such as the sodium salt sold by National Starch & Chemicals under the name Flexan 500 and 130.
- iii) Alkali metal or alkaline earth metal salts of sulphonic acids derived from lignin, and more particularly calcium lignosulphonates or sodium lignosulphonates, such as the product sold under the name Marasperse C-21 by American Can Co. and the C₁₀ to C₁₄ products sold by Avebene.
- iv) Polymers containing salified alkyl naphthalenesulphonic acid units, such as the sodium salt under the name Darvan No. 1 by Van der Bilt.

The anionic hair fixative polymers herein which include anionic monomers are preferably utilised in at least partially neutralised form in order to aid shampoo removability of the liquid hair cosmetic compositions. In the compositions the neutralisation of a polymer may be achieved by use of an inorganic base, preferably KOH. However organic base, preferably AMP (amino methyl propanol) and mixture of inorganic and organic base may also be used to effect the desired level of neutralisation in hair styling compositions. In total from

about 50% to about 100%, preferably from about 70% to about 100%, most preferably from about 80% to about 100% of the acidic monomers of each polymer utilised should be neutralised with base.

Any conventionally used base, organic or inorganic, may be used for neutralisation of acidic polymers provided they are utilised as specified herein. Hydroxides of alkali, alkaline earth and amino alcohols are suitable neutralisers.

Examples of suitable organic neutralizing agents which may be included in the compositions of the present invention include amines, especially amino alcohols such as 2-amino-2-methyl-1, 3-propanediol (AMPD), 2-amino-2ethyl-1, 3-propanediol (AEPD), 2-amino-2-methyl-1-propanol (AMP), 2-amino-1-butanol (AB), monethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), monoisopropanolamine (MIPA), diisopropanolamine (DIPA), triisopropanolamine (TIPA), dimethylsteramine (DMS) and amino methyl propanol (AMP) and mixtures thereof.

Preferred neutralising agents for use in hair care compositions of the present invention are potassium and sodium hydroxides.

Highly preferred anionic fixative polymers include commercially available material such as vinyl acetate/crotonic acid/vinyl neodecanoate copolymers and vinyl acetate/crotonic acid copolymers with the tradenames RESYN 28-2930, RESYN 28-2913, and RESYN 28-1310 supplied by National Starch & Chemicals, and acrylates copolymers and acrylates/acrylamide copolymers with tradenames LUVIMER 100P, ULTRAHOLD 8, and ULTRAHOLD STRONG supplied by BASF Corporation.

Nonionic Fixative Polymers

Nonionic fixative polymers useful herein are homopolymer of vinylpyrrolidone or vinylcaprolactum and copolymers of vinylpyrrolidone with vinylacetate such as those with tradenames LUVISKOL K grades and LUVISKOL VA grades supplied by BASF Corporation.

Silicone Grafted Copolymers

The silicone grafted copolymers useful herein include those which have a vinyl polymeric backbone (A and B monomers), and grafted to such backbone a polydimethylsiloxane macromer (C macromer) having a weight average molecular weight of from about 1,000 to about 50,000. Preferably, these copolymers contain from and from about 50.0% to about 99.9% of the combination of A and B monomers, and from about 0.1% to about 50.0% of C

- macromer, wherein A is a lipophilic, low polarity free radically polymerizable vinyl monomer, such as methacrylic or acrylic esters; B is a hydrophilic polar monomer which is copolymerizable with A, such as N,N-dimethylacrylamide, dimethylaminoethylmethacrylate, vinyl pyrrolidone, or quaternized dimethylaminoethyl methacrylate; and C is a silicone-containing macromer having a weight average molecular weight of from about 1,000 to about 50,000, based on polydimethylsiloxane. Preferred silicone grafted copolymers are those having a Tg above about -20°C, and a molecular weight of from about 10,000 to about 1,000,000.
- Suitable silicone grafted copolymers herein include those listed below wherein the numbers indicate the weight ratio of monomers and macromers in the copolymer, silicone macromer S1 is a dimethylpolysiloxane having a molecular weight of about 20,000, and silicone macromer S2 is a dimethylpolysiloxane having a molecular weight of about 10,000.
- 1) 20/63/17 acrylic acid/t-butyl methacrylate/silicone macromer S2, having a copolymer molecular weight about 100,000
 - 2) 10/70/20 dimethylacrylamide/isobutyl methacrylate/silicone macromer S2, having a copolymer molecular weight about 400,000
 - 3) 60/20/20 diallyldimethyl ammonium chloride/isobutyl methoacrylate/silicone macromer S2, having a copolymer molecular weight about 500,000
 - 4) 40/40/20 acrylic acid/methyl methacrylate/silicone macromer S1, having a copolymer molecular weight about 400,000
 - 5) 10/70/20 acrylic acid/t-butyl methacrylate/silicone macromer S1, having a copolymer molecular weight about 300,000
 - 6) 25/65/10 acrylic acid/isopropyl methacrylate/silicone macromer S2, having a copolymer molecular weight about 200,000
 - 7) 60/25/15 N,N'-dimethylacrylamide/methoxyethyl methacrylate/silicone macromer S1, having a copolymer molecular weight about 200,000
 - 8) 12/64/4/20 N,N'-dimethylacrylamide/isobutyl methacrylate/2-ethylhexyl methacrylate/silicone macromer S1, having a copolymer molecular weight about 300,000
 - 9) 30/40/10/20 N,N'-dimethylacrylamide/isobutyl methacrylate/2-ethylhexyl methacrylate/silicone macromer S1, having a copolymer molecular weight about 300,000

- 10) 80/20 t-butylacrylate/silicone macromer S2, having a copolymer molecular weight about 150,000

CARRIER

5 The styling composition of the present invention comprises a carrier. The level and species of the carrier are selected according to the compatibility with other components, and desired characteristic of the product. The styling compositions herein can be in any product form including, but not limited to, hair sprays, mists, mousses, gels, and creams.

10 The carrier useful in the present invention include water, volatile solvents, propellants, and mixtures thereof.

The water useful herein include deionized water and water from natural sources containing mineral cations. Deionized water is preferred.

15 Volatile solvents useful herein include lower alkyl alcohols having from 1 to 3 carbons, and hydrocarbons having from about 5 to about 8 carbons. The preferred volatile solvents are, ethanol, isopropanol, pentane, hexane, and heptane

20 Propellants may be used for mousse and hair spray product forms. Propellants, when used in the present invention, are selected depending on variables such as the remainder of components, the package, and whether the product is designed to be used standing or invert.

25 Propellants useful herein include fluorohydrocarbons such as difluoroethane 152a (supplied by DuPont), dimethylether, and hydrocarbons such as propane, isobutane, n-butane, mixtures of hydrocarbons such as LPG (liquefied petroleum gas), carbon dioxide, nitrous oxide, nitrogen, and compressed air.

EMULSIFYING SURFACTANT

30 The styling composition of the present invention may include an emulsifying surfactant to disperse the water insoluble components in the carrier. Water insoluble components may include hydrophobic fixative polymers mentioned above, and hydrophobic thickening polymers, high melting point conditioning agents, and oily conditioning agents mentioned below.

The level and species of the emulsifying surfactant are selected according to the compatibility with other components, and desired characteristic of the product. Emulsifying surfactants are selected from the group consisting of

nonionic surfactants, anionic surfactants, cationic surfactants, amphoteric surfactants, and mixtures thereof.

CONDITIONING AGENTS

5 The styling composition of the present invention may include a conditioning agent. Conditioning agents useful herein include high melting point compounds, oily compounds, silicone compounds, non-volatile solvents, and mixtures thereof.

High Melting Point Compound

10 The compositions may comprise a high melting point compound having a melting point of at least about 25°C selected from the group consisting of fatty alcohols, fatty acids, fatty alcohol derivatives, fatty acid derivatives, hydrocarbons, steroids, and mixtures thereof. Without being bound by theory, it is believed that these high melting point compounds cover the hair surface and reduce friction, thereby resulting in providing smooth feel on the hair and ease of
15 combing. It is understood by the artisan that the compounds disclosed in this section of the specification can in some instances fall into more than one classification, e.g., some fatty alcohol derivatives can also be classified as fatty acid derivatives. However, a given classification is not intended to be a limitation on that particular compound, but is done so for convenience of classification and nomenclature. Further, it is understood by the artisan that, depending on the
20 number and position of double bonds, and length and position of the branches, certain compounds having certain required carbon atoms may have a melting point of less than about 25°C. Such compounds of low melting point are not intended to be included in this section. Nonlimiting examples of the high melting
25 point compounds are found in International Cosmetic Ingredient Dictionary, Fifth Edition, 1993, and CTFA Cosmetic Ingredient Handbook, Second Edition, 1992, both of which are incorporated by reference herein in their entirety.

The fatty alcohols useful herein are those having from about 14 to about 30 carbon atoms, preferably from about 16 to about 22 carbon atoms. These
30 fatty alcohols can be straight or branched chain alcohols and can be saturated or unsaturated. Nonlimiting examples of fatty alcohols include, cetyl alcohol, stearyl alcohol, behenyl alcohol, and mixtures thereof.

The fatty acids useful herein are those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more
35 preferably from about 16 to about 22 carbon atoms. These fatty acids can be

straight or branched chain acids and can be saturated or unsaturated. Also included are diacids, triacids, and other multiple acids which meet the requirements herein. Also included herein are salts of these fatty acids. Nonlimiting examples of fatty acids include lauric acid, palmitic acid, stearic acid, behenic acid, sebacic acid, and mixtures thereof.

The fatty alcohol derivatives and fatty acid derivatives useful herein include alkyl ethers of fatty alcohols, alkoxyated fatty alcohols, alkyl ethers of alkoxyated fatty alcohols, esters of fatty alcohols, fatty acid esters of compounds having esterifiable hydroxy groups, hydroxy-substituted fatty acids, and mixtures thereof. Nonlimiting examples of fatty alcohol derivatives and fatty acid derivatives include materials such as methyl stearyl ether; the ceteth series of compounds such as ceteth-1 through ceteth-45, which are ethylene glycol ethers of cetyl alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; the steareth series of compounds such as steareth-1 through 10, which are ethylene glycol ethers of steareth alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; cetareth 1 through cetareth-10, which are the ethylene glycol ethers of cetareth alcohol, i.e. a mixture of fatty alcohols containing predominantly cetyl and stearyl alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; C₁-C₃₀ alkyl ethers of the ceteth, steareth, and cetareth compounds just described; polyoxyethylene ethers of behenyl alcohol; ethyl stearate, cetyl stearate, cetyl palmitate, stearyl stearate, myristyl myristate, polyoxyethylene cetyl ether stearate, polyoxyethylene stearyl ether stearate, polyoxyethylene lauryl ether stearate, ethyleneglycol monostearate, polyoxyethylene monostearate, polyoxyethylene distearate, propyleneglycol monostearate, propyleneglycol distearate, trimethylolpropane distearate, sorbitan stearate, polyglyceryl stearate, glyceryl monostearate, glyceryl distearate, glyceryl tristearate, and mixtures thereof.

Hydrocarbons useful herein include compounds having at least about 20 carbons.

Steroids useful herein include compounds such as cholesterol.

High melting point compounds of a single compound of high purity are preferred. Single compounds of pure fatty alcohols selected from the group of pure cetyl alcohol, stearyl alcohol, and behenyl alcohol are highly preferred. By "pure" herein, what is meant is that the compound has a purity of at least about

90%, preferably at least about 95%. These single compounds of high purity provide good rinsability from the hair when the consumer rinses off the composition.

Commercially available high melting point compounds useful herein include: cetyl alcohol, stearyl alcohol, and behenyl alcohol having tradenames KONOL series available from New Japan Chemical (Osaka, Japan), and NAA series available from NOF (Tokyo, Japan); pure behenyl alcohol having tradename 1-DOCOSANOL available from WAKO (Osaka, Japan), various fatty acids having tradenames NEO-FAT available from Akzo (Chicago Illinois, USA), HYSTRENE available from Witco Corp. (Dublin Ohio, USA), and DERMA available from Vevy (Genova, Italy); and cholesterol having tradename NIKKOL AGUASOME LA available from Nikko.

Oily Compound

The compositions comprise an oily compound having a melting point of not more than about 25°C selected from the group consisting of a first oily compound, a second oily compound, and mixtures thereof. The oily compounds useful herein may be volatile or nonvolatile. Without being bound by theory, it is believed that, the oily compounds may penetrate the hair to modify the hydroxy bonds of the hair, thereby resulting in providing softness and flexibility to the hair. The oily compound may comprise either the first oily compound or the second oily compound as described herein. Preferably, a mixture of the first oily compound and the second oily compound is used. The oily compounds of this section are to be distinguished from the high melting point compounds described above. Nonlimiting examples of the oily compounds are found in International Cosmetic Ingredient Dictionary, Fifth Edition, 1993, and CTFA Cosmetic Ingredient Handbook, Second Edition, 1992, both of which are incorporated by reference herein in their entirety.

First Oily Compound

The fatty alcohols useful herein include those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty alcohols can be straight or branched chain alcohols and can be saturated or unsaturated alcohols, preferably unsaturated alcohols. Nonlimiting examples of these compounds include oleyl alcohol, palmitoleic alcohol, isostearyl alcohol, isocetyl

alcohol, undecanol, octyl dodecanol, octyl decanol, octyl alcohol, caprylic alcohol, decyl alcohol and lauryl alcohol.

The fatty acids useful herein include those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty acids can be straight or branched chain acids and can be saturated or unsaturated. Suitable fatty acids include, for example, oleic acid, linoleic acid, isostearic acid, linolenic acid, ethyl linolenic acid, ethyl linolenic acid, arachidonic acid, and ricinolic acid.

The fatty acid derivatives and fatty alcohol derivatives are defined herein to include, for example, esters of fatty alcohols, alkoxylated fatty alcohols, alkyl ethers of fatty alcohols, alkyl ethers of alkoxylated fatty alcohols, and mixtures thereof. Nonlimiting examples of fatty acid derivatives and fatty alcohol derivatives, include, for example, methyl linoleate, ethyl linoleate, isopropyl linoleate, isodecyl oleate, isopropyl oleate, ethyl oleate, octyldodecyl oleate, oleyl oleate, decyl oleate, butyl oleate, methyl oleate, octyldodecyl stearate, octyldodecyl isostearate, octyldodecyl isopalmitate, octyl isopelargonate, octyl pelargonate, hexyl isostearate, isopropyl isostearate, isodecyl isononanoate, Oleth-2, pentaerythritol tetraoleate, pentaerythritol tetraisostearate, trimethylolpropane trioleate, and trimethylolpropane triisostearate.

Commercially available first oily compounds useful herein include: oleyl alcohol with tradename UNJECOL 90BHR available from New Japan Chemical, pentaerythritol tetraisostearate and trimethylolpropane triisostearate with tradenames KAKPTI and KAKTTI available from Kokyu Alcohol (Chiba, Japan), pentaerythritol tetraoleate having the same tradename as the compound name available from New Japan Chemical, trimethylolpropane trioleate with a tradename ENUJERUBU series available from New Japan Chemical, various liquid esters with tradenames SCHERCEMOL series available from Scher, and hexyl isostearate with a tradename HIS and isopropyl isostearate having a tradename ZPIS available from Kokyu Alcohol.

Second Oily Compound

The second oily compounds useful herein include straight chain, cyclic, and branched chain hydrocarbons which can be either saturated or unsaturated, so long as they have a melting point of not more than about 25°C. These hydrocarbons have from about 12 to about 40 carbon atoms, preferably from about 12 to about 30 carbon atoms, and preferably from about 12 to about 22

carbon atoms. Also encompassed herein are polymeric hydrocarbons of alkenyl monomers, such as polymers of C₂₋₆ alkenyl monomers. These polymers can be straight or branched chain polymers. The straight chain polymers will typically be relatively short in length, having a total number of carbon atoms as described
5 above. The branched chain polymers can have substantially higher chain lengths. The number average molecular weight of such materials can vary widely, but will typically be up to about 500, preferably from about 200 to about 400, and more preferably from about 300 to about 350. Also useful herein are the various grades of mineral oils. Mineral oils are liquid mixtures of
10 hydrocarbons that are obtained from petroleum. Specific examples of suitable hydrocarbon materials include paraffin oil, mineral oil, dodecane, isododecane, hexadecane, isohexadecane, eicosene, isoeicosene, tridecane, tetradecane, polybutene, polyisobutene, and mixtures thereof. Preferred for use herein are hydrocarbons selected from the group consisting of mineral oil, isododecane,
15 isohexadecane, polybutene, polyisobutene, and mixtures thereof.

Commercially available second oily compounds useful herein include isododecane, isohexadecane, and isoeicosene with tradenames PERMETHYL 99A, PERMETHYL 101A, and PERMETHYL 1082, available from Presperse (South Plainfield New Jersey, USA), a copolymer of isobutene and
20 normal butene with tradenames INDOPOL H-100 available from Amoco Chemicals (Chicago Illinois, USA), mineral oil with tradename BENOL available from Witco, isoparaffin with tradename ISOPAR from Exxon Chemical Co. (Houston Texas, USA), α -olefin oligomer with tradename PURESYN 6 from Mobil Chemical Co., and trimethylolpropane tricaprilate/tricaprate with tradename
25 MOBIL ESTER P43 from Mobil Chemical Co.

Silicone Compounds

The conditioning agents useful herein include silicone compounds. The silicone compounds hereof can include volatile soluble or insoluble, or nonvolatile soluble or insoluble silicone conditioning agents. By soluble what is meant is that
30 the silicone compound is miscible with the carrier of the composition so as to form part of the same phase. By insoluble what is meant is that the silicone forms a separate, discontinuous phase from the carrier, such as in the form of an emulsion or a suspension of droplets of the silicone.

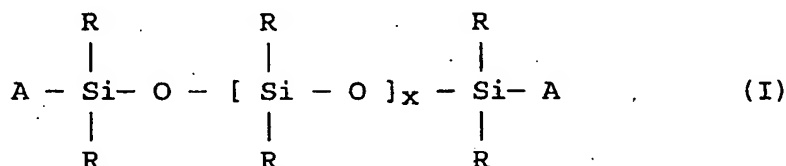
Suitable silicone fluids include polyalkyl siloxanes, polyaryl siloxanes,
35 polyalkylaryl siloxanes, polyether siloxane copolymers, and mixtures thereof.

Other nonvolatile silicone compounds having hair conditioning properties can also be used.

The silicone compounds herein also include polyalkyl or polyaryl siloxanes with the following structure (I)

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wherein R is alkyl or aryl, and x is an integer from about 7 to about 8,000. "A" represents groups which block the ends of the silicone chains. The alkyl or aryl groups substituted on the siloxane chain (R) or at the ends of the siloxane chains (A) can have any structure as long as the resulting silicone remains fluid at room temperature, is dispersible, is neither irritating, toxic nor otherwise harmful when applied to the hair, is compatible with the other components of the composition, is chemically stable under normal use and storage conditions, and is capable of being deposited on and conditions the hair. Suitable A groups include hydroxy, methyl, methoxy, ethoxy, propoxy, and aryloxy. The two R groups on the silicon atom may represent the same group or different groups. Preferably, the two R groups represent the same group. Suitable R groups include methyl, ethyl, propyl, phenyl, methylphenyl and phenylmethyl. The preferred silicone compounds are polydimethylsiloxane, polydiethylsiloxane, and polymethylphenylsiloxane. Polydimethylsiloxane, which is also known as dimethicone, is especially preferred. The polyalkylsiloxanes that can be used include, for example, polydimethylsiloxanes. These silicone compounds are available, for example, from the General Electric Company in their ViscasilR and SF 96 series, and from Dow Corning in their Dow Corning 200 series.

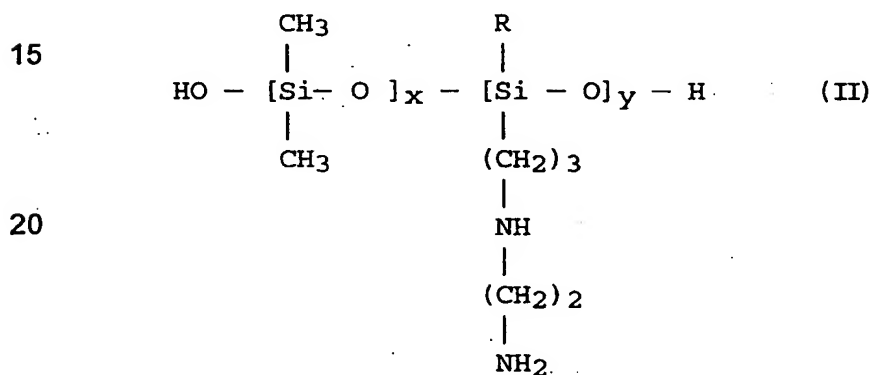
Polyalkylaryl siloxane fluids can also be used and include, for example, polymethylphenylsiloxanes. These siloxanes are available, for example, from the General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid.

Especially preferred, for enhancing the shine characteristics of hair, are highly arylated silicone compounds, such as highly phenylated polyethyl silicone having refractive index of about 1.46 or higher, especially about 1.52 or higher. When these high refractive index silicone compounds are used, they should be

mixed with a spreading agent, such as a surfactant or a silicone resin, as described below to decrease the surface tension and enhance the film forming ability of the material.

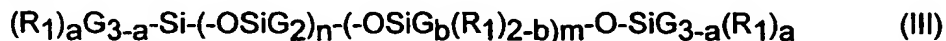
The silicone compounds that can be used include, for example, a polypropylene oxide modified polydimethylsiloxane although ethylene oxide or mixtures of ethylene oxide and propylene oxide can also be used. The ethylene oxide and polypropylene oxide level should be sufficiently low so as not to interfere with the dispersibility characteristics of the silicone. These material are also known as dimethicone copolyols.

Other silicone compounds include amino substituted materials. Suitable alkylamino substituted silicone compounds include those represented by the following structure (II)



wherein R is CH₃ or OH, x and y are integers which depend on the molecular weight, the average molecular weight being approximately between 5,000 and 10,000. This polymer is also known as "amodimethicone".

Suitable amino substituted silicone fluids include those represented by the formula (III)



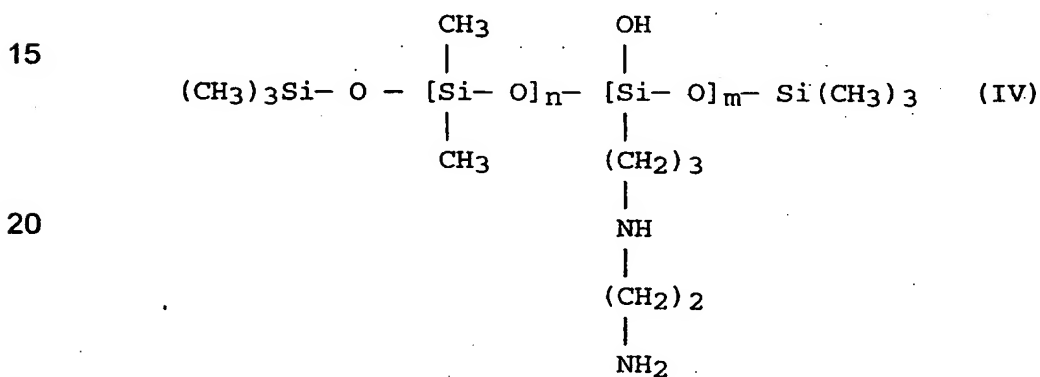
in which G is chosen from the group consisting of hydrogen, phenyl, OH, C₁-C₈ alkyl and preferably methyl; a denotes 0 or an integer from 1 to 3, and preferably equals 0; b denotes 0 or 1 and preferably equals 1; the sum n+m is a number from 1 to 2,000 and preferably from 50 to 150, n being able to denote a number from 0 to 1,999 and preferably from 49 to 149 and m being able to denote an integer from 1 to 2,000 and preferably from 1 to 10; R₁ is a monovalent radical

of formula $C_qH_{2q}L$ in which q is an integer from 2 to 8 and L is chosen from the groups

- N(R₂)CH₂-CH₂-N(R₂)₂
- N(R₂)₂
- 5 -N(R₂)₃A⁻
- N(R₂)CH₂-CH₂-NR₂H₂A⁻

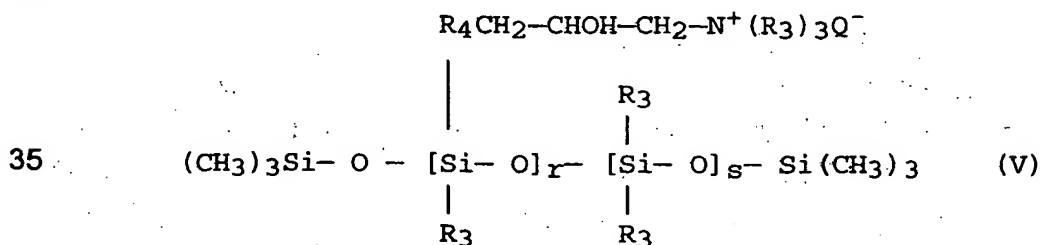
in which R₂ is chosen from the group consisting of hydrogen, phenyl, benzyl, a saturated hydrocarbon radical, preferably an alkyl radical containing from 1 to 20 carbon atoms, and A⁻ denotes a halide ion.

- 10 An especially preferred amino substituted silicone corresponding to formula (III) is the polymer known as "trimethylsilylamodimethicone", of formula (IV):



In this formula n and m are selected depending on the exact molecular weight of the compound desired.

Other amino substituted silicone polymers which can be used are represented by the formula (V):



- where R³ denotes a monovalent hydrocarbon radical having from 1 to 18 carbon atoms, preferably an alkyl or alkenyl radical such as methyl; R₄ denotes a

hydrocarbon radical, preferably a C₁ - C₁₈ alkylene radical or a C₁ - C₁₈; and more preferably C₁ - C₈, alkyleneoxy radical; Q⁻ is a halide ion, preferably chloride; r denotes an average statistical value from 2 to 20, preferably from 2 to 8; s denotes an average statistical value from 20 to 200, and preferably from 20 to 50. A preferred polymer of this class is available from Union Carbide under the name "UCAR SILICONE ALE 56."

References disclosing suitable nonvolatile dispersed silicone compounds include U.S. Patent No. 2,826,551, to Geen; U.S. Patent No. 3,964,500, to Drakoff, issued June 22, 1976; U.S. Patent No. 4,364,837, to Pader; and British Patent No. 849,433, to Woolston, all of which are incorporated herein by reference in their entirety. Also incorporated herein by reference in its entirety is "Silicon Compounds" distributed by Petrarch Systems, Inc., 1984. This reference provides an extensive, though not exclusive, listing of suitable silicone compounds.

Another nonvolatile dispersed silicone that can be especially useful is a silicone gum. The term "silicone gum", as used herein, means a polyorganosiloxane material having a viscosity at 25°C of greater than or equal to 1,000,000 centistokes. It is recognized that the silicone gums described herein can also have some overlap with the above-disclosed silicone compounds. This overlap is not intended as a limitation on any of these materials. Silicone gums are described by Petrarch, and others including U.S. Patent No. 4,152,416, to Spitzer et al., issued May 1, 1979 and Noll, Walter, Chemistry and Technology of Silicones, New York: Academic Press 1968. Also describing silicone gums are General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76. All of these described references are incorporated herein by reference in their entirety. The "silicone gums" will typically have a mass molecular weight in excess of about 200,000, generally between about 200,000 and about 1,000,000. Specific examples include polydimethylsiloxane, poly(dimethylsiloxane methylvinylsiloxane) copolymer, poly(dimethylsiloxane diphenylsiloxane methylvinylsiloxane) copolymer and mixtures thereof.

Also useful are silicone resins, which are highly crosslinked polymeric siloxane systems. The crosslinking is introduced through the incorporation of tri-functional and tetra-functional silanes with mono-functional or di-functional, or both, silanes during manufacture of the silicone resin. As is well understood in the art, the degree of crosslinking that is required in order to result in a silicone

resin will vary according to the specific silane units incorporated into the silicone resin. In general, silicone materials which have a sufficient level of trifunctional and tetrafunctional siloxane monomer units, and hence, a sufficient level of crosslinking, such that they dry down to a rigid, or hard, film are considered to be silicone resins. The ratio of oxygen atoms to silicon atoms is indicative of the level of crosslinking in a particular silicone material. Silicone materials which have at least about 1.1 oxygen atoms per silicon atom will generally be silicone resins herein. Preferably, the ratio of oxygen:silicon atoms is at least about 1.2:1.0. Silanes used in the manufacture of silicone resins include monomethyl-, dimethyl-, trimethyl-, monophenyl-, diphenyl-, methylphenyl-, monovinyl-, and methylvinylchlorosilanes, and tetrachlorosilane, with the methyl substituted silanes being most commonly utilized. Preferred resins are offered by General Electric as GE SS4230 and SS4267. Commercially available silicone resins will generally be supplied in a dissolved form in a low viscosity volatile or nonvolatile silicone fluid. The silicone resins for use herein should be supplied and incorporated into the present compositions in such dissolved form, as will be readily apparent to those skilled in the art. Without being bound by theory, it is believed that the silicone resins can enhance deposition of other silicone compounds on the hair and can enhance the glossiness of hair with high refractive index volumes.

Other useful silicone resins are silicone resin powders such as the material given the CTFA designation polymethylsilsequioxane, which is commercially available as TospearlTM from Toshiba Silicones.

The method of manufacturing these silicone compounds, can be found in Encyclopedia of Polymer Science and Engineering, Volume 15, Second Edition, pp 204-308, John Wiley & Sons, Inc., 1989, which is incorporated herein by reference in its entirety.

Silicone materials and silicone resins in particular, can conveniently be identified according to a shorthand nomenclature system well known to those skilled in the art as the "MDTQ" nomenclature. Under this system, the silicone is described according to the presence of various siloxane monomer units which make up the silicone. Briefly, the symbol M denotes the mono-functional unit $(\text{CH}_3)_3\text{SiO}_{1.5}$; D denotes the difunctional unit $(\text{CH}_3)_2\text{SiO}$; T denotes the trifunctional unit $(\text{CH}_3)\text{SiO}_{1.5}$; and Q denotes the quadri- or tetra-functional unit SiO_2 . Primes of the unit symbols, e.g., 'M', 'D', 'T', and 'Q' denote substituents

other than methyl, and must be specifically defined for each occurrence. Typical alternate substituents include groups such as vinyl, phenyl, amino, hydroxyl, etc. The molar ratios of the various units, either in terms of subscripts to the symbols indicating the total number of each type of unit in the silicone, or an average thereof, or as specifically indicated ratios in combination with molecular weight, complete the description of the silicone material under the MDTQ system. Higher relative molar amounts of T, Q, T' and/or Q' to D, D', M and/or M' in a silicone resin is indicative of higher levels of crosslinking. As discussed before, however, the overall level of crosslinking can also be indicated by the oxygen to silicon ratio.

The silicone resins for use herein which are preferred are MQ, MT, MTQ, MQ and MDTQ resins. Thus, the preferred silicone substituent is methyl. Especially preferred are MQ resins wherein the M:Q ratio is from about 0.5:1.0 to about 1.5:1.0 and the average molecular weight of the resin is from about 1000 to about 10,000.

Non-volatile solvents

Non-volatile solvents useful herein include alkyl alcohols having more than 3 carbons, and polyhydric alcohols. The polyhydric alcohols useful herein include 1,2-propane diol or propylene glycol, 1,3-propane diol, hexylene glycol, glycerin, diethylene glycol, dipropylene glycol, 1,2-butylene glycol, and 1,4-butylene glycol.

THICKENING POLYMER

The compositions may include a thickening polymer. Thickening polymers are preferred for hair gel. When present, the thickening polymer functions as a viscosity-building agent, and can be distinguished from the fixative polymers mentioned above. The thickening polymer will generally comprise from about 0.1% to about 10.0%, and more typically from about 0.2% to about 3.0%, by weight, of the composition.

Useful thickening polymers herein include crosslinked carboxyvinyl polymers. Preferred among these polymers are the copolymers of acrylic acid crosslinked with polyallylsucrose as described in U.S. Patent 2,798,053, which is incorporated herein by reference in its entirety. Examples of these polymers include the carbomers, which are homopolymers of acrylic acid crosslinked with an allyl ether of pentaerythritol, an allyl ether of sucrose, or an allyl ether of propylene. Other preferred thickening polymers include the cross-linked

copolymers of methyl vinyl ether and maleic acid. Examples of these polymers include Stabilezes. Preferred carboxyvinyl polymers have a molecular weight of at least about 750,000; more preferred are carboxyvinyl polymers having a molecular weight of at least about 1,250,000; most preferred are carboxyvinyl
5 polymers having a molecular weight of at least about 3,000,000.

Other thickening polymers useful herein include those that can impart a gel-like viscosity to the composition, such as water soluble or colloiddally water soluble polymers like cellulose ethers such as hydroxyethyl cellulose and
10 hydrophobically modified cellulose, and materials such as guar gum, xanthan gum, polyvinyl alcohol, polyvinyl pyrrolidone, hydroxypropyl guar gum, starch and starch derivatives.

ADDITIONAL COMPONENTS

A wide variety of other additional ingredients can be formulated into the present compositions. These include: other conditioning agents such as
15 hydrolyzed collagen with tradename Peptin 2000 available from Hormel, Vitamin E with tradename Emix-d available from Eisai, panthenol available from Roche, panthenyl ethyl ether available from Roche, hydrolysed keratin, proteins, plant extracts, and nutrients; preservatives such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; pH adjusting agents, such as
20 citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide, sodium carbonate; salts, in general, such as potassium acetate and sodium chloride; coloring agents, such as any of the FD&C or D&C dyes; hair oxidizing (bleaching) agents, such as hydrogen peroxide, perborate and persulfate salts; hair reducing agents such as the thioglycolates; perfumes; and sequestering
25 agents, such as disodium ethylenediamine tetra-acetate. Such optional ingredients generally are used individually at levels from about 0.001% to about 10.0%, preferably from about 0.01% to about 5.0% by weight of the composition.

EXAMPLES

30 The following examples further describe and demonstrate embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations thereof are possible without departing from the spirit and scope of the invention. Ingredients are identified by chemical or CTFA
35 name, or otherwise defined below.

Compositions

	Ex1	Ex2	Ex3	Ex4	Ex5	Ex6
Optical Brightener 1 *1	0.20	-	-	-	-	-
Optical Brightener 2 *2	-	0.25	-	-	-	-
Optical Brightener 3 *3	-	-	0.50	-	-	-
Optical Brightener 4 *4	-	-	-	0.20	-	-
Optical Brightener 5 *5	-	-	-	-	1.00	-
Optical Brightener 6 *6	-	-	-	-	-	0.15
Ultrahold 8 *13	6.00	-	-	-	0.50	-
Copolymer 937 *14	-	2.00	-	-	-	1.25
Amphomer LV71 *17	-	-	2.00	-	-	-
Yukaformer R205 *18	-	-	-	2.00	1.50	-
Aminomethyl propanol	0.15	-	0.30	-	0.04	-
Lauramide DEA	0.10	-	-	0.10	-	0.05
Triisopropylamine	-	-	-	0.10	-	-
Dimethicone Copolyol SH3746 *19	0.10	-	-	-	-	0.05
Perfume	0.20	0.20	0.10	0.10	0.20	0.20
DI Water	20.0	45.5	20.0	45.0	21.0	46.0
Isobutane/propane blend	25.0	25.0	25.0	-	15.0	-
Dimethyl ether	-	-	-	35.0	-	-
Hydrolyzed Collagen *33	0.01	-	-	-	-	-
Vitamin E *34	0.01	-	-	-	-	-
Panthenol *35	0.025	-	-	-	-	-
Panthenyl Ethyl Ether *36	0.225	-	-	-	-	-
Ethanol	—————q.s. to 100%—————					

	Ex7	Ex8	Ex9	Ex10	E11
Optical Brightener 2 *2	-	-	-	0.15	-
Optical Brightener 3 *3	-	-	-	-	0.20
Optical Brightener 6 *6	-	-	-	-	0.10
Optical Brightener 7 *7	0.25	-	-	0.05	-
Optical Brightener 8 *8	-	0.65	-	-	-
Optical Brightener 9 *9	-	-	0.20	-	-

Copolymer 937 *14	-	-	-	-	0.50
Luviskol VA64 *15	-	-	-	-	1.50
Luviquat PQ 11 *16	0.50	1.00	-	-	-
Amphomer LV71 *17	1.50	-	0.50	-	-
Yukaformer R205 *18	-	1.00	-	-	-
Silicone-grafted copolymer 1 *10	-	-	1.50	2.00	-
Aminomethyl propanol	0.18	-	0.10	-	-
Lauramide DEA	-	0.10	-	-	0.05
Triisopropylamine	0.05	-	-	-	0.05
Dimethicone Copolyol SH3746 *19	-	-	-	-	0.10
Perfume	0.10	0.10	0.20	0.10	0.10
DI Water	20.0	20.0	20.0	45.0	-
Isobutane/propane blend	-	15.0	25.0	-	-
Dimethyl ether	35.0	-	-	-	35.0
Ethanol	—————q.s. to 100%—————				

	Ex12	Ex13	Ex14	Ex15	Ex16
Optical Brightener 1 *1	0.20	-	-	-	-
Optical Brightener 2 *2	-	0.25	-	-	-
Optical Brightener 3 *3	-	-	0.50	-	-
Optical Brightener 4 *4	-	-	-	0.20	-
Optical Brightener 5 *5	-	-	-	-	1.00
Ultrahold Strong *20	1.00	-	-	-	-
Copolymer 845 *21	-	2.00	-	-	-
Luviquat PQ 11 *16	-	-	-	-	0.50
Amphomer 28-4910 *23	-	-	4.00	-	-
Yukaformer 510 *24	2.00	2.00	-	3.00	-
Celquat L-200 *25	-	-	-	-	2.50
Aminomethyl propanol	0.15	-	0.70	-	-
Laureth-23	0.25	-	0.20	0.10	-
Laureth-7	-	0.20	0.10	0.10	-
Stearyltrimethyl ammonium chloride	-	-	-	-	0.20
Dimethicone Copolyol SH3746 *19	0.10	-	-	-	-

DC BY22-009 *26	0.15	-	-	0.10	-
Propylene glycol	0.10	0.25	0.10	-	0.25
Methylparaben	0.15	0.15	0.10	0.10	0.15
Perfume	0.20	0.20	0.10	0.10	0.20
Ethanol	-	12.5	7.50	-	10.0
Isobutane/propane blend	6.00	8.00	7.00	10.0	8.00
Deionized Water	—————q.s. to 100%—————				

	Ex17	Ex18	Ex19	Ex20	Ex21
Optical Brightener 2 *2	-	-	-	-	0.15
Optical Brightener 6 *6	0.15	-	-	-	-
Optical Brightener 7 *7	-	0.25	-	-	0.05
Optical Brightener 8 *8	-	-	0.65	-	-
Optical Brightener 9 *9	-	-	-	0.20	-
Luviskol VA 73 W *22	-	-	1.00	-	-
Luviquat PQ 11 *16	1.25	0.50	3.00	-	-
Amphomer 28-4910 *23	-	2.50	-	0.50	-
Yukaformer 510 *24	1.25	-	-	1.00	3.00
Celquat L-200 *25	-	-	-	-	0.50
Silicone-grafted copolymer 2 *11	-	-	-	1.50	-
Aminomethyl propanol	-	0.50	-	0.10	-
Laureth-23	0.15	-	0.10	-	0.25
Laureth-7	-	-	-	0.25	-
Stearyltrimethyl ammonium chloride	-	0.15	-	-	-
Dimethicone Copolyol SH3746 *19	0.05	-	-	-	-
DC BY22-009 *26	-	-	0.20	-	-
Propylene glycol	0.10	-	0.20	0.05	-
Methylparaben	0.15	0.10	0.15	0.10	-
Perfume	0.20	0.10	0.10	0.20	0.10
Ethanol	6.00	15.0	-	2.50	5.50
Isobutane/propane blend	8.00	7.00	9.00	-	8.00
Deionized Water	—————q.s. to 100%—————				

	Ex22	Ex23	Ex24	Ex25	Ex26
Optical Brightener 1 *1	0.20	-	-	-	-
Optical Brightener 2 *2	-	0.25	-	-	-
Optical Brightener 3 *3	-	-	0.50	-	-
Optical Brightener 4 *4	-	-	-	0.20	-
Optical Brightener 5 *5	-	-	-	-	1.00
Gantrez ES-255 *37	1.00	-	-	-	-
Copolymer 958 *27	-	2.00	-	-	-
Luviquat PQ 11 *16	-	-	-	-	0.50
Amphomer 28-4910 *23	-	-	4.00	-	-
Yukaformer SM *28	2.00	1.00	-	3.00	-
Celquat H-100 *25	-	-	-	-	2.50
Aminomethyl propanol	0.15	-	0.70	-	-
Carbopol 940 *29	1.00	-	0.50	-	-
Stabileze 06 *30	-	0.25	-	0.50	-
Cellosize HEC QP *31	-	-	-	-	1.50
Sodium hydroxide	0.28	0.04	0.14	0.08	-
Laureth-23	0.25	-	0.20	-	0.25
Oleth-20	-	0.20	-	-	-
Dimethicone Copolyol SH3746 *19	0.10	-	0.05	-	-
Methylparaben	0.15	0.15	0.10	0.10	0.15
Tetrasodium EDTA	0.10	0.05	0.10	0.10	-
Perfume	0.10	0.15	0.10	0.10	0.20
Ethanol	-	-	6.00	-	2.00
Deionized Water	q.s. to 100%				

	Ex27	Ex28	Ex29	Ex30	Ex31
Optical Brightener 2 *2	-	-	-	-	0.15
Optical Brightener 6 *6	0.15	-	-	-	-
Optical Brightener 7 *7	-	0.25	-	-	0.05
Optical Brightener 8 *8	-	-	0.65	-	-
Optical Brightener 9 *9	-	-	-	0.20	-
Copolymer 958 *27	1.25	-	-	-	-
Luviskol VA64 *15	-	-	1.00	-	-

Luviquat PQ 11 *16	-	0.50	3.00	-	-
Amphomer 28-4910 *23	-	2.50	-	0.50	-
Yukaformer SM *28	1.25	-	-	1.00	3.00
Celquat H-100 *25	-	-	-	-	0.50
Silicone-grafted copolymer 3 *12	-	-	-	1.50	-
Aminomethyl propanol	-	0.50	-	0.10	-
Carbopol 940 *29	-	0.50	-	-	0.25
Stabileze 06 *30	-	-	-	1.00	-
Poly Surf 67 *32	1.25	-	1.00	-	-
Sodium hydroxide	-	0.14	-	0.16	0.07
Laureth-23	0.15	-	0.10	-	0.25
Oleth-20	0.15	0.25	-	-	-
Dimethicone Copolyol SH3746 *19	0.05	-	-	-	-
Methylparaben	0.15	0.10	0.15	0.10	-
Tetrasodium EDTA	0.10	0.10	0.10	-	0.10
Perfume	0.20	0.10	0.10	0.20	0.10
Ethanol	4.00	1.50	-	2.50	5.50
DI Water	—————q.s. to 100%—————				

Definitions

- *1 Optical Brightener 1: 1,4-bis(2-cyanostyryl)benzene
- *2 Optical Brightener 2: 6,7-dihydroxy coumarin
- 5 *3 Optical Brightener 3: 4-methyl-7-hydroxy coumarin
- *4 Optical Brightener 4: 4,4'-bis(5-methylbenzoxazol-2-yl)stilbene
- *5 Optical Brightener 5: 2,4-dimethoxy-6-(1'-pyrenyl)-1,3,5-triazine
- *6 Optical Brightener 6: porphyrin
- *7 Optical Brightener 7: 4,4'-bis[(4-anilino-6-methylamino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonic acid
- 10 *8 Optical Brightener 8: 4,4'-bis[(4-anilino-6-ethylamino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonic acid
- *9 Optical Brightener 9: 4,4'-bis[(4-anilino-6-(2-hydroxyethyl)methylamino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonic acid
- 15 *10 Silicone grafted copolymer 1: 20/63/17 acrylic acid/t-butyl methacrylate/silicone macromer S2, polymer molecular weight about 100,000

- *11 Silicone grafted copolymer 2: 25/65/10 acrylic acid/isopropyl methacrylate/silicone macromer S2, polymer molecular weight about 200,000
- 5 *12 Silicone grafted copolymer 3: 60/25/15 N,N'-dimethylacrylamide/methoxyethyl methacrylate/silicon macromer S1, polymer molecular weight about 200,000
- *13 Ultrahold 8: Copolymer of acrylic acid, ethyl acrylate, and N-t-butyl acrylamide commercially available from BASF.
- 10 *14 Copolymer 937: Copolymer of vinylpyrrolidone and dimethylaminoethyl methacrylate, commercially available from ISP.
- *15 Luviskol VA64: Copolymer of vinylpyrrolidone and vinyl acetate, commercially available from BASF.
- 15 *16 Luvisquat PQ 11: Copolymer of vinylpyrrolidone and N,N'-dimethylaminoethyl methacrylate diethyl sulfate salt, commercially available from BASF.
- *17 Amphomer LV71: Copolymer of octylacrylamide, alkyl acrylates, butylaminoethyl methacrylate, commercially available from National Starch and Chemical Company.
- 20 *18 Yukaformer R205: Copolymer of methoacryloyl ethyl betaine and alkyl acrylates, commercially available from Mitsubishi Chemical Corporation.
- *19 Dimethicone Copolyol SH3746: Polydimethylsiloxane with polyoxyethylene side chain.
- *20 Ultrahold Strong: Copolymer of acrylic acid, ethyl acrylate, and N-t-butyl acrylamide, commercially available from BASF.
- 25 *21 Copolymer 845: Copolymer of vinylpyrrolidone and dimethylaminoethyl methacrylate, commercially available from ISP.
- *22 Luviskol VA 73W: Copolymer of vinylpyrrolidone and vinyl acetate, commercially available from BASF.
- 30 *23 Amphomer 28-4910: Copolymer of octylacrylamide, alkyl acrylates, butylaminoethyl methacrylate, commercially available from National Starch and Chemical Company.
- *24 Yukaformer 510: Copolymer of methoacryloyl ethyl betaine and alkyl acrylates, commercially available from Mitsubishi Chemical Corporation.

- *25 Celquat L-200 and Celquat H-100: Versions of copolymers of hydroxyethylcellulose and dimethyldiallylammonium chloride, commercially available from National Starch and Chemical Company.
- *26 DC BY22-009: Silicone microemulsion commercially available from Dow Corning.
- *27 Copolymer 958: Copolymer of vinylpyrrolidone and dimethylaminoethyl methacrylate, commercially available from ISP.
- *28 Yukaformer SM: Copolymer of methoacryloyl ethyl betaine and alkyl acrylates, commercially available from Mitsubishi Chemical Corporation.
- *29 Carbopol 940: Cross-linked polyacrylic acid, commercially available from B.F. Goodrich.
- *30 Stabileze 06: Cross-linked copolymer of methyl vinyl ether and maleic acid, commercially available from ISP.
- *31 Cellosize HEC QP: Hydroxyethyl cellulose.
- *32 Poly Surf 67: Hydrophobically modified hydroxyethyl cellulose commercially available from Aqualon Co.
- *33 Hydrolyzed Collagen: Peptin 2000 from Hormel
- *34 Vitamin E: Emix-d from Eisai
- *35 Panthenol: from Roche
- *36 Panthenyl Ethyl Ether : from Roche
- *37 Gantrez ES-225: Copolymer of vinyl methyl ether and ethyl ester of maleic acid, commercially available from ISP.

Method of Preparation

The hair spray products of Examples 1 through 8 are suitably made as follows: Hair fixative polymer is dissolved in a portion of water and ethanol. In case an anionic fixative polymer such as Ultrahold 8 is used, it is neutralized with aminomethylpropanol in a portion of water and ethanol. To this is added the remaining components except isobutane/propane blend. The obtained mixture is mixed until homogeneous. Finally, the concentrate thus obtained is packed into an aerosol can with isobutane/propane blend.

The hair mousse products of Examples 12 through 21 are suitably made as follows: Hair fixative polymer is dissolved in a portion of water. In case an anionic fixative polymer such as Ultrahold Strong is used, it is neutralized with aminomethylpropanol in a portion of water. To this is added the remaining ingredients except isobutane/propane blend. The obtained mixture is mixed until

homogeneous. The concentrate thus obtained is packed into an aerosol can with isobutane/propane blend.

5 The hair setting gel products of Examples 22 through 31 are suitably made as follows: Carbopol 940 is dissolved in a portion of water. To this is added sodium hydroxide. In a separate container, the remaining components are dissolved in a portion of water. The two premixes are blended with agitation.

Examples 1 through 31 have many advantages. For example, they can be used daily, and provide color alteration, shininess, and UV protection to the hair.

10 It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to one skilled in the art without departing from its spirit and scope.

WHAT IS CLAIMED IS:

1. A hair styling composition comprising:
 - (a) an effective amount of an optical brightener selected from the group consisting of a nonionic optical brightener, an amphoteric optical brightener and mixtures thereof;
 - 5 (b) a fixative polymer selected from the group consisting of an amphoteric fixative polymer, an anionic fixative polymer, a cationic fixative polymer, a nonionic fixative polymer, a silicone grafted copolymer, and mixtures thereof; wherein the 3% aqueous solution of the fixative polymer provides a viscosity of no more than about
10 2,000 cps; and
 - (c) a carrier suitable for hair.
2. The hair styling composition according to Claim 1 wherein the optical brightener is selected from the group consisting of polystyrylstilbenes, triazinstilbenes, hydroxycoumarins, triazoles, pyrazolines, oxazoles, pyrenes, porphyrins, and mixtures thereof.
3. The hair styling composition according to Claim 1 comprising by weight from about 0.001% to about 20% of the optical brightener; and from about 0.01% to about 10% of the fixative polymer.
4. The hair styling composition according to Claim 3 wherein the fixative polymer comprises by weight from about 0.1% to about 5% of a betainized amphoteric fixative polymer; and from about 0.1% to about 5% of a non-betainized amphoteric fixative polymer.
5. The hair styling composition according to Claim 3 wherein the fixative polymer comprises by weight from about 0.1% to about 5% of an amphoteric fixative polymer; and from about 0.1% to about 5% of an anionic fixative polymer.
6. The hair styling composition according to Claim 3 wherein the fixative polymer comprises by weight from about 0.1% to about 5% of an

amphoteric fixative polymer; and from about 0.1% to about 5% of a cationic fixative polymer.

7. The hair styling composition according to Claim 3 wherein the fixative polymer comprises by weight from about 0.1% to about 5% of a cationic fixative polymer; and from about 0.1% to about 5% of a nonionic fixative polymer.
8. The hair styling composition according to any of Claims 1 through 7 further comprising an emulsifying surfactant.
9. The hair styling composition according to any of Claims 1 through 7 further comprising a conditioning agent.
10. The hair styling composition according to any of Claims 1 through 7 further comprising a thickening polymer.
11. The hair styling composition according to Claim 4 wherein the composition comprises no more than about 30% by weight of a volatile solvent, and wherein the composition is substantially free of propellant.

INTERNATIONAL SEARCH REPORT

Int'l Application No

PCT/US 97/16313

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K7/13 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 312 855 A (GRAND PAUL S) 26 January 1982 cited in the application see column 1, line 9-20 see column 2, line 11-64 see column 5, line 45 - column 6, line 14; claims; example 11; table III	1-3,7-11
Y	GB 2 307 639 A (GEN ELECTRIC) 4 June 1997 cited in the application see claims 1-4	1-11

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Orviz Diaz, P

INTERNATIONAL SEARCH REPORT

Int lional Application No

PCT/US 97/16313

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CA 1 255 603 A (COSMEPRO INC LAB) 13 June 1989 cited in the application see page 3, line 7 - page 4, line 9 see page 1, line 29 - page 2, line 2; claim 7 -----	1-11
Y	GB 1 328 108 A (UNILEVER LTD) 30 August 1973 cited in the application see page 1, line 10-17 see page 1, line 65-92; claims 1,6 -----	1-11
Y	GB 1 368 316 A (OREAL) 25 September 1974 see example 7 -----	1-11
Y	US 3 723 616 A (ERLEMAN G ET AL) 27 March 1973 see column 6, line 14-25 -----	1-11
Y	WO 97 18795 A (OREAL ;AUDOUSSET MARIE PASCALE (FR); MONDET JEAN (FR)) 29 May 1997 see page 4, line 28-32; claims; example 2 -----	1-11

INTERNATIONAL SEARCH REPORT

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